DECONTAMINATION OF SOILS BY ACTIVATION WITH ACIDS AND BASES

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DECLARATION

I, the undersigned, hereby declare that the work contained in this Masters thesis is my own original work and that I have not previously in its entirety or in part submitted it at any university for a degree

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ABSTRACT

DECONTAMINATION OF SOIL BY ACTIVATION WITH ACIDS AND BASES

New, more receptive surfaces can be generated in soils by a partial dissolution of existing, crystalline solids followed by re-precipitation as poorly crystalline colloids with a larger capacity to adsorb ionic and molecular contaminants. This priming process can be carried out by treating the soil with strong acid or base and then neutralising it again. The aim of this study was to investigate the effectiveness of acid and base treatments in reducing inorganic contaminant availability in different soil types.

The first study involved investigating the change in cation (cadmium[II], copper[II]) and anion (phosphate) sorption of four different soils before and after priming. Hydrochloric acid and KOH were used to adjust the pH of soils to below pH 2 or above pH 12 in the dissolution stage of the priming treatment. After neutralisation it was found that base priming resulted in an increase in metal cation adsorption in all the soils, most notably in the sesquioxidic (increase from 19.5 to 73.5 mmol $Cd.kg^{-1}$ soil) and kaolinitic soils (from 16.9 to 38.3 mmol $Cd.kg^{-1}$ soil), whereas acid priming decreased it or had little effect on cation sorption. However, acid priming increased anion sorption in all soil types, to a greater extent than base priming, most notably in the organic soil (from 6.3 to 14.7 mmol $PO_4.kg^{-1}$ soil). This can be attributed to the differences in the nature of the precipitate (more aluminous or alumino-siliceous) depending on whether the dissolution was carried out in acid or basic conditions, and the final pH of the soil solution, as the hydroxyaluminium and hydroxyaluminosilicate precipitates which form are known to enhance pH-dependent sorption of metals.

In the second study, the soil was suspended in Cd or Cu solutions and then the pH was adjusted to below 2 or above 12 using HCl or KOH. After 5 days of shaking the pH was adjusted to a neutral pH again. The availability of the Cd and Cu was determined at each of the stages in the treatment, and it was found that both the acid and base treatments were effective in removing Cu from solution, whereas only the base treatment was effective in removing Cd. Determinations were also carried out using H_2SO_4 and $Ca(OH)_2$ and it was found that they were equally effective. It can be proposed that this acid-base pair would be

of most practical importance as the salt generated is gypsum which is generally considered benign, and can actually help to improve the soil structure.

Activation of soils by acid or base conditioning could have some useful applications in decontaminating soils or decreasing the mobility of inorganic contaminants in soils. Primed soils could also be used as cheap absorbents for decontaminating water.

UITTREKSEL

DEKONTAMINERING VAN GROND DEUR AKTIVIERING MET SURE EN BASISE

Nuwe, meer ontvanklike oppervlakke kan in gronde gegenereer word deur middel van gedeeltelike oplossing van bestaande, kristallyne vaste stowwe gevolg deur herpresipitasie as swak kristallyne kolloïede met 'n groter kapasiteit om ioniese en molekulêre kontaminante te adsorbeer. Hierdie behandelingsproses kan uitgevoer word deur die grond met sterk suur of basis te behandel en dit daarna te neutraliseer. Die doel van hierdie studie was om die effektiwiteit van suur- of basisbehandelings om anorganiese kontaminante te verminder, in verskillende grond tipes te ondersoek.

Die eerste studie het die ondersoek na die verandering in katioon- (kadmium[II], koper[II]) en anioon- sorpsie (fosfaat) van vier verskillende gronde voor en na suur of basis voorbehandeling behels. Soutsuur en KOH was gebruik om die pH van die gronde tot onder pH 2 of bo pH 12 aan te pas gedurende die oplosstadium van die behandelingsproses. Na neutralisasie is dit gevind dat basis voorbehandeling tot 'n toename in metaal katioonadsorpsie in al die gronde gelei het, en dit was veral waarneembaar in die seskwioksied (toename van 19.5 tot 73.5 mmol $Cd.kg^{-1}$ grond) en kaolinitiese (van 16.9 tot 38.3 mmol $Cd.kg^{-1}$ grond) gronde, terwyl suur voorbehandeling dit verlaag het of 'n klein effek op katioonsorpsie gehad het. Suur voorbehandeling, egter, het anioonsorpsie in al die gronde verhoog, tot 'n groter mate as basis voorbehandeling, veral in die organiese grond (van 6.3 tot 14.7 mmol fosfaat.kg^{-1} grond). Dit kan toegeskryf word aan die verskille in die aard van die neerslag wat meer aluminium- of aluminiumsilika-ryk kan wees afhangede of die oplossing uitgevoer was in suur of basis kondisies, en ook die finale pH van die grondoplossing omdat die hidroksi-aluminium en hidroksi-aluminiumsilikaat presipitate wat vorm bekend daarvoor is om pH-afhanklike sorpsie van metale te bevorder.

In die tweede studie, was die grond in Cd- of Cu-oplossings gesuspendeer en die pH was aangepas tot onder 2 of bo 12 met HCl of KOH. Na vyf dae van skud was die pH weer aangepas tot by neutraal. Die beskikbaarheid van Cd en Cu was bepaal by elke stadium in die behandeling, en dit is gevind dat beide suur- en basisbehandeling meer effektief was in die verwydering van Cu uit oplossing, terwyl slegs die basisbehandeling effektief was in die

verwydering van Cd. Bepalings was ook uitgevoer met die gebruik van H_2SO_4 en $Ca(OH)_2$ en dit is gevind dat dit net so doeltreffend was soos HCl en KOH. Dit kan voorgestel word dat hierdie suur-basis paar in die praktyk belangriker sal wees omdat die sout wat gegenereer word, nl. gips, as 'n gunstige sout beskou word.

Aktivering van grond deur suur- of basis-kondisionering kan sekere bruikbare toepassings in die dekontaminering van gronde hê of dit kan gebruik word om die mobiliteit van anorganiese kontaminante te verlaag. Suur of basis voorbehandelde gronde kan ook gebruik word as goedkoop absorbante vir die dekontaminering van water.

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INTRODUCTION

Soils become contaminated both accidentally and deliberately. In either case it is usually desirable to minimise the mobility of the contaminants if these pose a threat to the quality of the environment. Soil surface properties can be modified in terms of both adsorptive surface area and the nature and strength of ionic and covalent bonding between adsorbed solutes and colloid surfaces.

The rationale for this study is that new, more receptive surfaces can be generated in soils by a partial dissolution of existing, crystalline solids followed by re-precipitation as poorly crystalline colloids with a larger capacity to adsorb ionic and molecular contaminants. Such a strategy is identical in principle to that of conventional water purification with alum and lime, except that the opportunity for producing a scavenging precipitate could be pursued in either direction on the acid-base scale. An aluminous hydroxide precipitate with ferric and other metal impurities might be expected through acid addition followed by neutralisation with lime. On the other hand a more siliceous product might result from base addition followed by neutralisation with acid. The fresh precipitates would coat existing surfaces, occlude contaminants, and probably enhance reactive surface area and the capacity to adsorb fresh contaminants. Opportunities for cleaning up old waste disposal sites and for protecting groundwater from new ones can be contemplated. The objective of this project is to explore the variety of precipitates that can be formed by such acid-base priming of soils and the capacity of such precipitates to reduce the mobility of solutes of environmental interest.

The main question is the following: Will harsh acid or base treatment of soils produce new, more reactive surfaces with the capacity to immobilize environmental contaminants?

This question is founded upon the following three sub-hypotheses, namely that:

1. Acid-base treatment will increase the specific surface area of the soil by generating new colloidal solids.

2. The new solids will possess relatively clean surfaces available for adsorption of metals and ligands either as covalent inner-sphere complexes or as outer-sphere cations or anions.

3. New solids that form during neutralisation of treated soils will co-precipitate with other solutes (e.g. metal ions by induced hydrolysis).

Additional questions that also need to be addressed are:

- Will the buffer capacity (pH-dependent charge) be affected?
- In what way will initial soil colloid composition (e.g. smectitic or kaolinitic clay, sesquioxidic clay or humic substances) affect the character of new solids precipitated?
- Will acidification produce different solids from those formed via an alkaline treatment route?
- To what extreme pH should the soil be adjusted and for how long in order to generate a significant change in surface properties and contaminant immobilisation?
- What difference does it make when different acids (sulphuric or hydrochloric) or alkalis (sodium or calcium hydroxide, for example) are employed for the priming treatment and/or subsequent neutralisation?
- Could such treatments be applied practically in a field situation?

The first part of the project was conducted at the Institute for Land Evaluation and Soil Science at the University of Hohenheim, Stuttgart, Germany. It was decided that the acid and base priming effects should be investigated on four contrasting soil types as their responses should differ quite significantly due to differences in mineralogy and organic matter content. Thus four already well characterised soil samples were chosen from the Institute's soil store, namely a smectitic and organic soil from Germany and a sesquioxidic and kaolinitic soil from Thailand.

As the proposed treatments investigated in this project initially involve dissolving the soil under extreme pH conditions, in Chapter 1 the acid- and base-dissolution kinetics of the four chosen soils were studied. The dissolution of Al, Si and Fe from the soils in strong solutions of HCl and KOH was determined using ICP-OES, and the change in pH was also observed. This was carried out in order to compare the dissolution reaction of the different soils, as well as to find the optimal equilibration time and optimal concentration of acid or base to release a considerable amount of Al. The acid-base pair, HCl and KOH, was used throughout this study, except for the last experiment in Chapter 3.

In the Chapter 2, the change in the chemical characteristics due to acid- or base-priming was investigated in the four soils already studied in chapter one. Sorption studies using the metals, cadmium(II) and copper(II) were carried out at University of Hohenheim on the acid- and base-primed soils, as well as on untreated soil.

The remaining experimental work in Chapter 2 was conducted at the Department of Soil Science, Stellenbosch University, South Africa. This included a phosphate sorption study carried out on the treated and untreated soils. The BET external specific surface area was also determined in two of the treated soils, to observe if there was any change due to acid or base priming. Surface charge determinations were also carried out on all of the primed and un-primed soils.

In Chapter 3 the effect of acid or base treatments on the solubility of Cd and Cu in soils contaminated with these metals was investigated. In the first experiment, conducted at University of Hohenheim, Cd and Cu availability in solution was compared on the smectitic and kaolinitic soils studied in Chapter 1, at three stages during the acid and base treatment. The second part of the study was conducted at Stellenbosch University, where two South African soils were used. A vertic topsoil (Arcadia form) and a kaolinitic subsoil (Griffin form - Soil Classification Working Group, 1991) were chosen. Copper solubility was investigated on these two acid- and base-treated soils as in the first experiment, however the effectiveness of the acid-base pair, H_2SO_4 and $Ca(OH)_2$, was compared with HCl and KOH.

With these relatively simple experiments it was hoped to answer some of the above mentioned questions, and to demonstrate the principle of acid and base priming soils.

Chapter 1

1 SOIL DISSOLUTION USING STRONG ACID OR BASE

1.1 Introduction

As both proposed treatments investigated in this project involved initially dissolving the soil under extreme pH conditions, it was essential to know how different soil types react to harsh acid and base treatments over time. It was decided that the acid and base priming effects should be investigated on four contrasting soil types as their responses should differ quite significantly due to differences in mineralogy and organic matter content.

Specifically, I wanted to know what the optimal acid or base equilibration period would be, and which concentrations of acid or base would suffice to release a reasonable amount of Al or Si to see a change in the soils' chemical characteristics. It was also clear that acid and base dissolution result in different reaction products, which has important implications for the precipitates formed from these products. Thus the amount of Al, Si and Fe released from the various soils over time was compared between the acid and base treatments.

Most of the literature published on dissolution of soils deals with acid dissolution, specifically with the concerns of acid rain and its impact on the environment. It is understandable as there are hardly any extremely alkaline soils found in nature, whereas acid sulfate soils and soils affected by acid mine drainage frequently occur. This also means that this study is unique in that it compares the acid and base dissolution of different soils using equally strong acids (HCl) and bases (KOH) of the same molarity. The following literature review looks at the buffering reactions of soils, and at some of the work that has been published on the effect of different acids on soil dissolution.

1.1.1 Soil buffering

The soil consists of various components all of which respond differently to an extreme shift in soil pH. Ulrich (1991) presented a useful summary of how these components operate together in buffering pH (Fig 1.1).

Buffer substance	pH range	Main reaction product (chemical change in soil)
Carbonate buffer range		
$CaCO_3$	8.6 > pH > 6.2	$Ca(HCO_3)_2$ in solution
Silicate buffer range		
Primary silicates	Whole pH scale (dominating buffer reaction in CO_3 free soils pH > 5)	Clay minerals (increase in CEC)
Cation exchange buffer range		
Clay minerals	5 > pH > 4.2	Non-exchangeable $n[Al(OH)_x^{(3-x)+}]$ (blockage of permanent charge, reduction of CEC)
Mn oxides		Exchangeable Mn^{2+} (reduction of base saturation)
Clay minerals		Exchangeable Al^{3+} (reduction of base saturation)
Interlayer Al $n[Al(OH)_x^{(3-x)+}]$		Al hydroxy-sulfates (accumulation of acid in case of H_2SO_4 input)
Aluminum buffer range		
Interlayer Al	4.2 > pH	Al^{3+} in solution (Al displacement, reduction in permanent charge)
Al hydroxy-sulfates		
Aluminum / iron buffer range		
Like Al buffer range in addition: "Soil $Fe(OH)_3$"	3.8 > pH	Exchangeable H^+ + Fe Organic Fe complexes (Fe displacement, bleaching)
Iron buffer range		
Ferrihydrite	3.2 > pH	Exchangeable H^+ + Fe (Fe displacement, bleaching, clay destruction)

Figure 1.1 Buffer systems and their pH ranges in soil (Ulrich, 1991)

1.1.2 Silicates

Alkali and alkali-earth silicates are the first group to undergo acid dissolution in the pH range above 4. Below pH 4.2 aluminosilicates start to undergo dissolution. Senkayi *et al.* (1981) found that silicate minerals undergo dissolution under extremely acid pH conditions in the following order: chlorite > smectite > mica > kaolinite. The review of Ritchie (1994) looked specifically at the factors that influence dissolution and precipitation of Al containing

minerals under acidic conditions. McBride (1994) has summarised the basic principles involved in silicate dissolution. Al is more soluble than Si in acid solutions. The solutions rapidly become saturated with Si as the Al continues to dissolve, without the structural framework of the aluminosilicate breaking down (McKeague *et al.,* 1963). At equilibrium in the acid and neutral pH ranges, Si is found as $Si(OH)_4^0$ (monosilicic acid). Super-saturation results in the formation of colloidal solutions of amorphous silica, consisting of $Si(OH)_4^0$ polymers. Alumina solubility is, however, influenced by the fact that $Al(OH)_3$ is amphoteric. In alkaline solutions, Al and Si solubility increases with pH. At high pH values Al is soluble as the $Al(OH)_4^-$ anion, and is thus tetrahedrally coordinated. Si is most soluble in the form of silicate, $Si(OH)_3^-$, which forms above pH 9 (McBride, 1994).

1.1.3 Metal oxides and hydroxides

In the neutral to slightly acidic pH range the metal oxides and hydroxides (predominantly of Al, Mn and Fe) can become protonated. Below pH 4 the oxides and hydroxides undergo dissolution (Bruggenwert *et al.*, 1991). As mentioned before, Al becomes increasingly soluble at alkaline pH (especially above pH 11) as the $Al(OH)_4^-$ ion. Fe and Mn oxides are stable at high pH, as only trace quantities of $Fe(OH)_4^-$ and $Mn(OH)_3^-$ come into in solution (Lindsay, 1979).

1.1.4 Exchangeable anions and cations

Exchangeable cations and anions are likely to be of little quantitative importance against the more considerable quantities of dissolving solids in strongly acidic or alkaline conditions. The acid or base added to the soil will determine the dominant anion or cation in the product.

1.1.5 Carbonates

The carbonates are the first group of minerals to undergo acid dissolution, from about pH 8.5 downwards (McBride, 1994). Acid neutralisation reactions generate bicarbonate salts. Carbonate minerals are stable at highly alkaline pH values (Lindsay, 1979).

1.1.6 Organic matter

Soil humus contains a variety of acidic functional groups with relatively low pK_a values which, when dissociated, have a high affinity for complexing Al^{3+} and Fe^{3+}, and to a lesser extent certain other metal cations, depending on which type of functional groups are present on the organic matter (Harter *et al.*, 1995). Al^{3+} can force a larger degree of dissociation of humus, especially since it binds quite strongly (McBride, 1994). Organic matter can thus interfere to some extent with the solubility of Al and other metal cations in solution, retarding the precipitation of metal hydroxides. At high pH values the metal-organic complexes dissolve and humus becomes dispersed.

1.1.7 Effect of type of acid

Yeoh and Oades (1981a & b) studied the effect of nitric and phosphoric acid on soil and soil clays. They also investigated the effect that the neutralisation of the added acid had on the structure of the soil. They found that phosphoric acid was more efficient than nitric acid of the same molarity in dissolution of clays in a closed system. H_3PO_4 released considerably more Al from kaolinite than HNO_3. When the reaction products from the acidification with phosphoric acid were precipitated in the presence of clay, they were shown to exist as an aluminium phosphate containing amorphous silica. They concluded that phosphoric acid treatment of soil should improve the aggregation of soils by supplying interstitial cements of aluminium phosphate and silica.

Marion et al. (1989) investigated the effect of extreme HCl deposition on soil. They proposed that acid neutralisation takes place in two steps. Initially there is a direct exchange of H^+ for basic cations and an interchange reaction between surface H^+ and structural Al. In the second step there is an indirect exchange through H^+ neutralisation by polyhydroxyl-Al complexes with concurrent base displacement. Eventually a pure acidic (H-Al) complex develops. Under very acidic conditions acid neutralisation is primarily controlled by mineral dissolution via the acidic cations (H^+ and Al^{3+}).

Xu and Ji (2001) investigated the difference in the effect on acidification and aluminium species between H_2SO_4 and HNO_3 on two contrasting soil types. They found that H_2SO_4 had a weaker effect on the acidification of variable charge soils, due to the specific adsorption of

SO_4^{2-} and the accompanied release of OH^-. They found for constant charge soils that the difference between the acids was small.

1.1.8 Conclusions

In order to dissolve sufficient Al for the precipitation of new solids, the pH of the soil solution should be maintained below 4 or above 11. Silica is most soluble at alkaline pH. If the formation of a predominantly aluminosilicate is desired, dissolution should be carried out at an extreme alkaline pH. HCl and KOH were chosen as the acid-base pair in these experiments, specifically as the counter ions do not easily form complexes with reaction products, and would not interfere in the dissolution process or with the precipitation of the reaction products.

1.2 Materials and methods

The four soils that were chosen from the well-catalogued soil store of the University of Hohenheim, Stuttgart, consisted of a smectitic and an organic rich soil from Germany, and a sesquioxidic and kaolinitic soil from Thailand (Table 1.1). These four soils were used in the majority of the experiments conducted in this project. These samples had already been extensively described and characterised, saving much time and allowing for immediate commencement of the dissolution and other acid base priming investigations.

The German soil samples, namely the organic and smectitic soils, came from Oberer Lindenhof and Wurmlingen, Baden-Württemberg, respectively. The organic topsoil (*Terra Fusca* form - Arbeitsgemeinschaft Bodenkunde, 1994), came from a fir forest, while the smectitic subsoil sample (*Pelosol* form - Arbeitsgemeinschaft Bodenkunde, 1994), came from a pasture field. Detailed information about these two soils can be found at www.uni-hohenheim.de/bodenatlas-bawue. The Thai samples, namely the kaolinitic and sesquioxidic subsoil samples, came from Mae Sa Noi and Pang Ma Pha, respectively. Fig. 1.2 shows the x-ray diffractograms of the kaolinitic and sesquioxidic soils.

Table 1.1 Summary of the characteristics of the Hohenheim soils.

Soil (catalogue no.)	pH H_2O	% C	% Clay	% $CaCO_3$	CEC ($cmol_c.kg^{-1}$)	Fe_{ed} ($g.kg^{-1}$)	Fe eo/ed	Dominant clay minerals
Organic (1211)	5.1	8.9	43	0	26.6	21.5	0.24	65% kaolinite, 35% illite
Smectitic (1443)	7.1	1.9	51	3	24.7	10.0	0.43	60% illite, 40% smectite
Sesquioxidic (15525)	6.2	0.7	83	0	11.0	-	0.02	50% gibbsite, 15% hematite, kaolinite
Kaolinitic (14943)	5.4	0.7	52	0	10.0	-	0.01	90% kaolinite

eo = oxalate extraction; ed = dithionate extraction

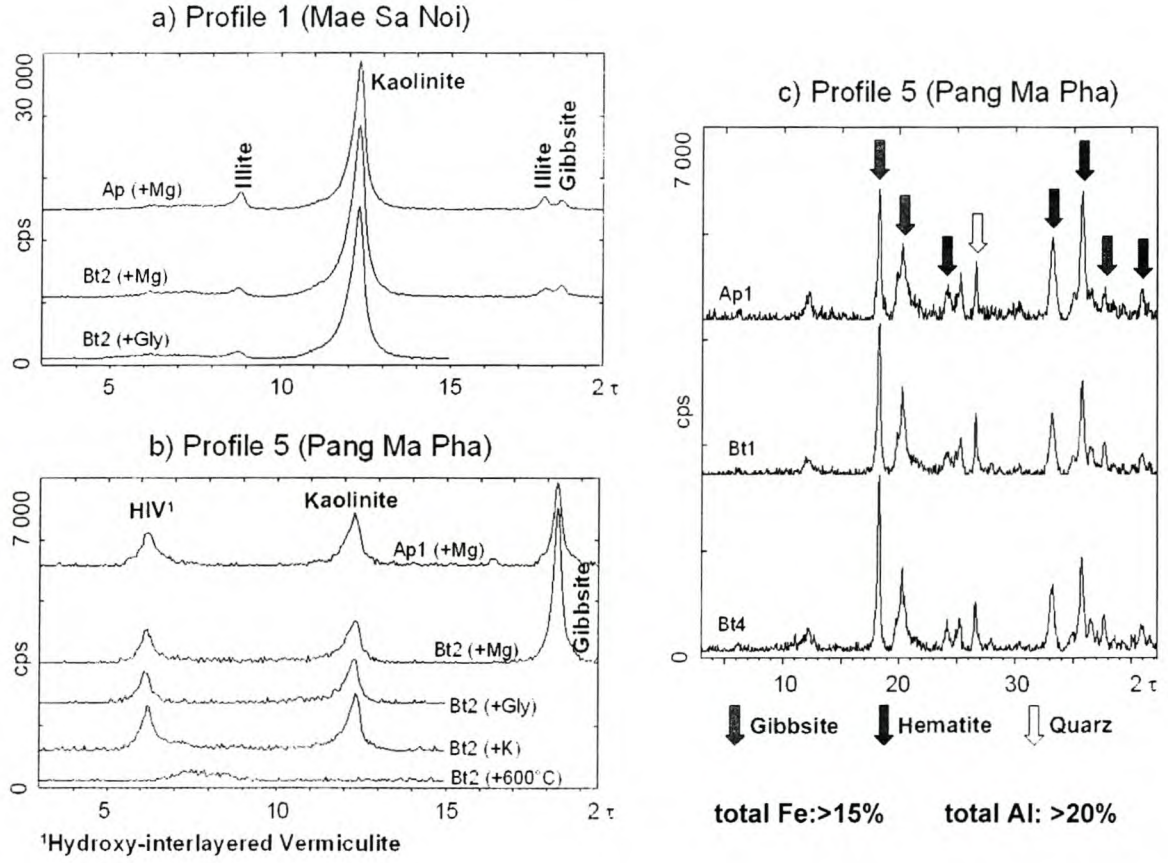


Figure 1.2 X-ray diffractograms of clay fraction of the kaolinitic sample (profile 1) and the sesquioxidic sample (profile 5). (Courtesy of Dr L. Herrmann, University of Hohenheim)

Initially the four chosen soils were titrated (Mettler DL21) with 0.05 M HCl or KOH to obtain an idea of how much acid or base to add to the soils to obtain a pH below 2 or above 12. It was found that 1:10 soil to solution suspension with 0.1 M HCl or KOH brought the pH values of the soils into the required pH range.

Acid and base equilibrations were carried out on all four Hohenheim soils using 0.1 M HCl or 0.1 M KOH. For the equilibration, 50 ml KOH or HCl was added to 5g soil and shaken very gently in a sealed polyethylene bottle, so as to avoid sedimentation. There was a replicate for each sampling interval, namely 12 hours, 1 day, 7 days, 14 days and 35 days. Each of these replicates was terminated at the specified time and the pH was measured, and the suspension was centrifuged to separate the soil from the solution. The solution was then filtered using Watman no. 640d filter paper. The concentrations of Al, Fe and Si were then determined in the solutions using ICP-OES (Varian Vista Pro) equipped with a CCD spray chamber, a Meinhard type nebulizer and external calibration.

1.3 Results and discussion

Figs. 1.3 – 1.6 show the dissolution of Al, Si and Fe ($mmol.kg^{-1}$ soil) from each of the four soils equilibrated with 0.1 M HCl or 0.1 M KOH over a period of 5 weeks.

In general the acid equilibration resulted in a greater dissolution of Al and Si, than the base equilibration, except in the case of the kaolinitic soil (Fig. 1.5), where similar amounts of Al and Si were released. The most dramatic difference between the release of Al and Si between the acid and base equilibrations can be seen in the smectitic soil (Fig. 1.3). The difference between the Al released is approximately seven-fold (120:16 $mmol.kg^{-1}$) and for Si release approximately four-fold (60:16 $mmol.kg^{-1}$) between acid and base equilibrations, respectively.

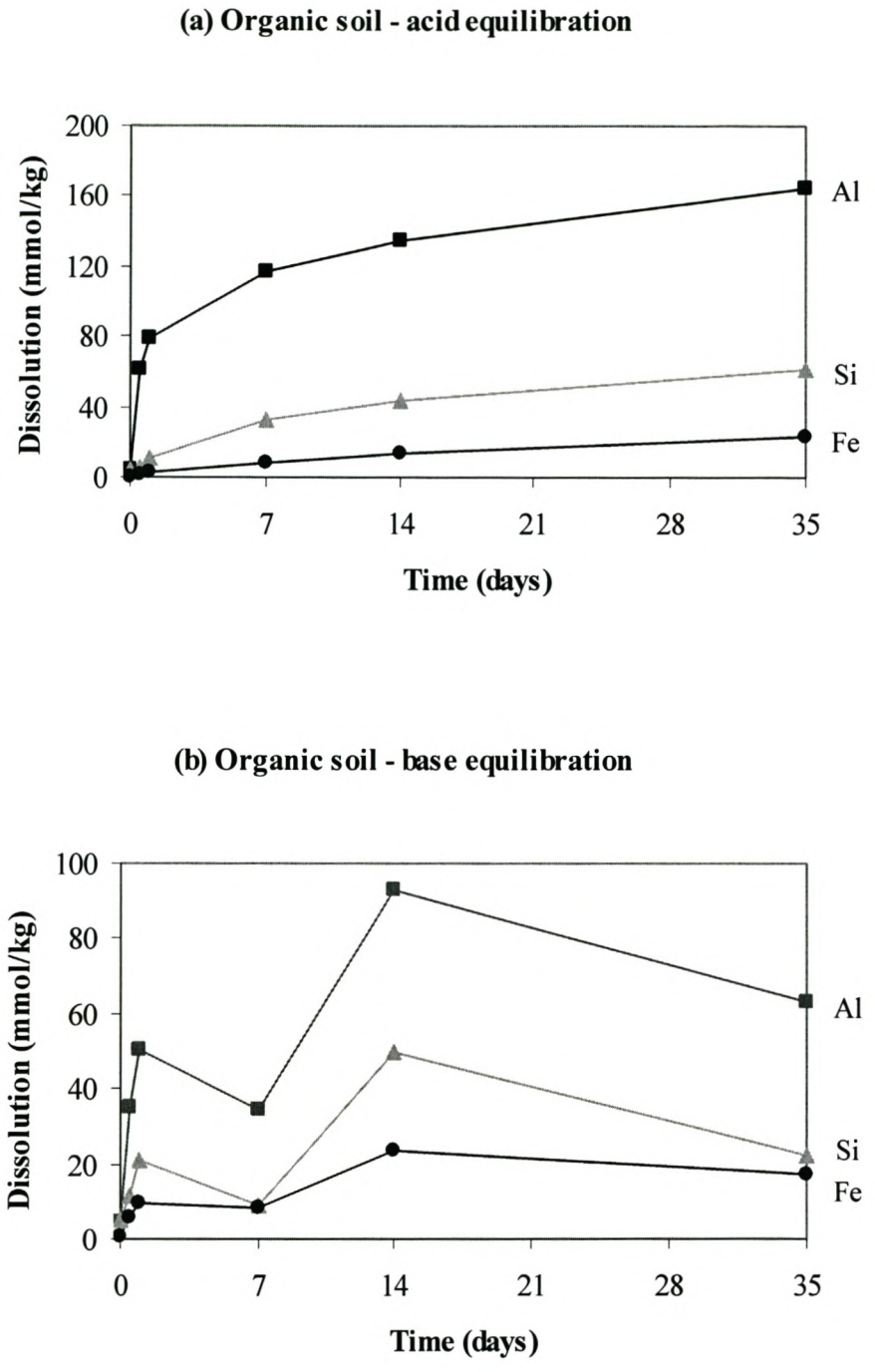


Figure 1.3 Dissolution (expressed per unit mass of soil) of Al, Si and Fe over time during the (a) acid and (b) base equilibration of the organic soil.

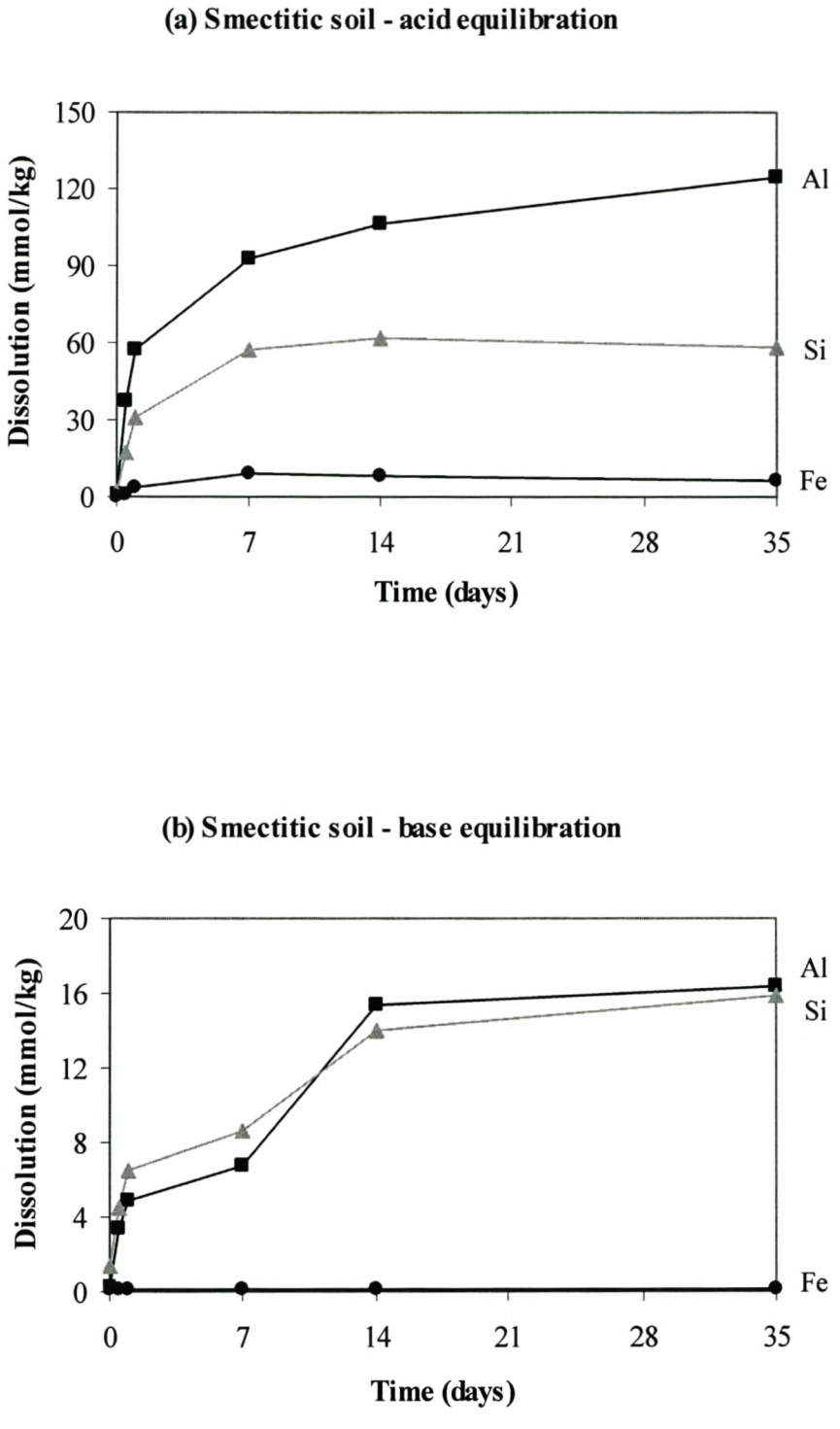


Figure 1.4 Dissolution (expressed per unit mass of soil) of Al, Si and Fe over time during the (a) acid and (b) base equilibration of the smectitic soil.

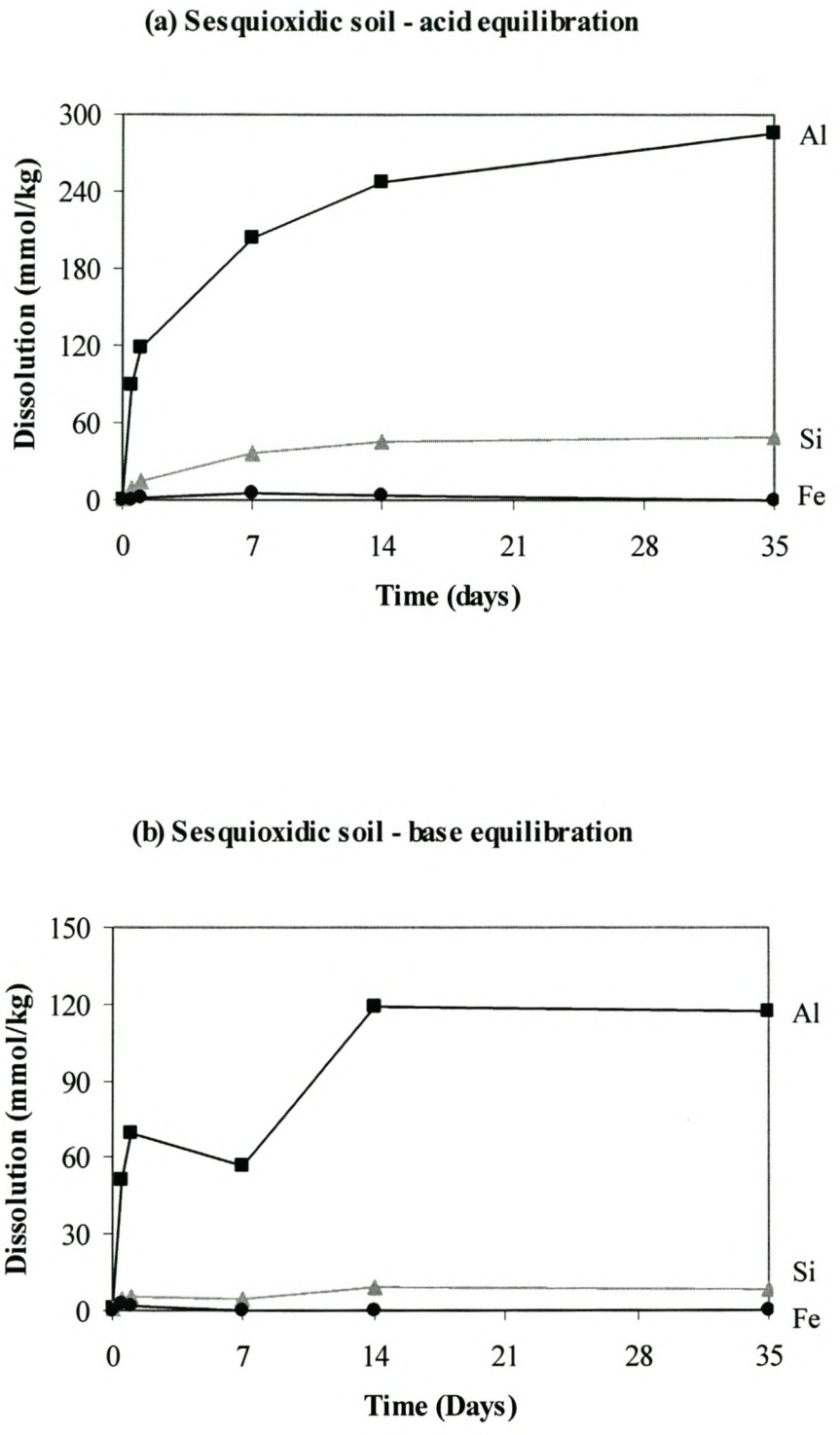


Figure 1.5 Dissolution (expressed per unit mass of soil) of Al, Si and Fe over time during the (a) acid and (b) base equilibration of the sesquioxidic soil.

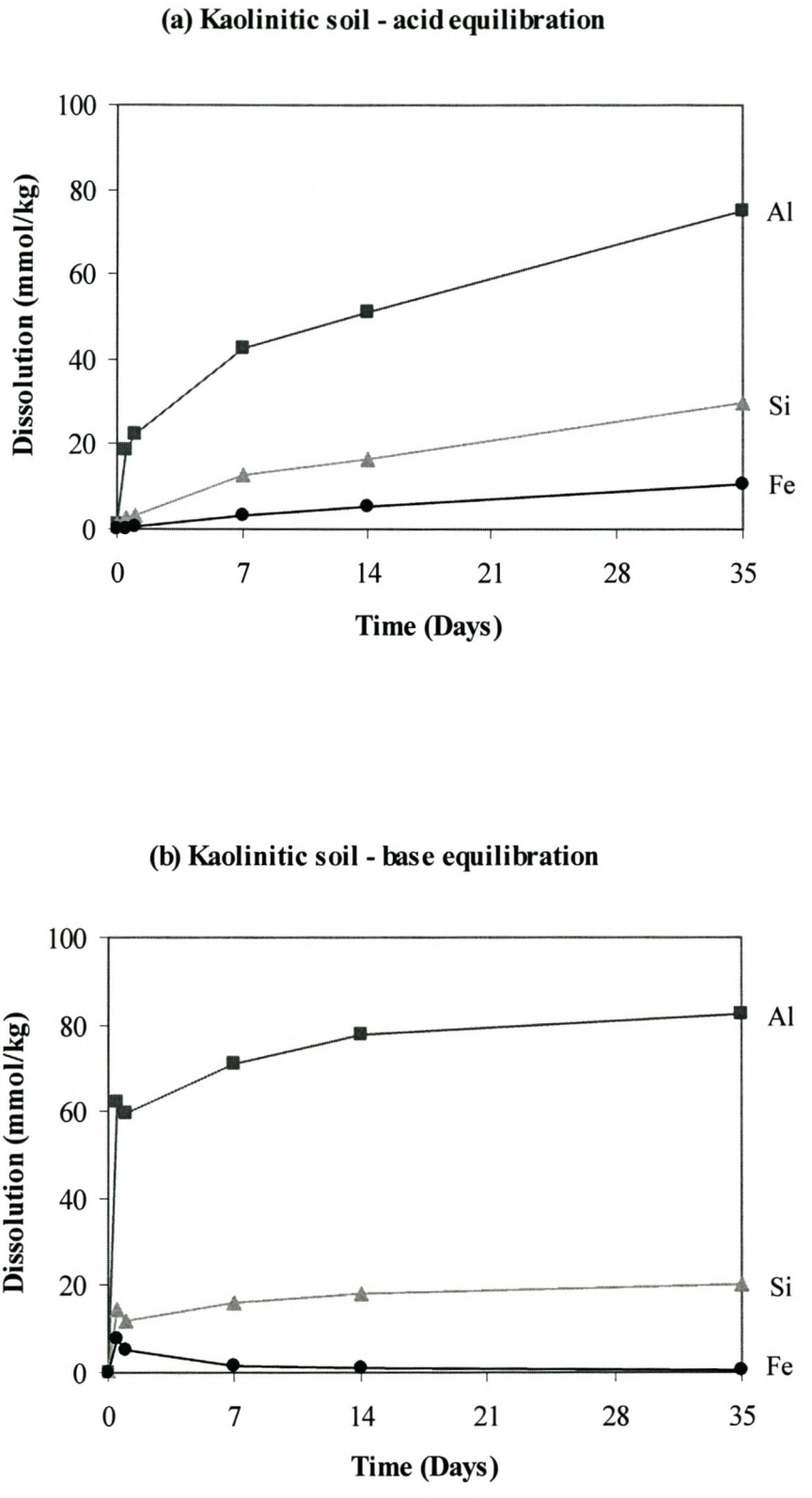


Figure 1.6 Dissolution (expressed per unit mass of soil) of Al, Si and Fe over time during the (a) acid and (b) base equilibration of the kaolinitic soil.

Since acid dissolution is proton driven, while base dissolution is hydroxyl driven, the difference in the size of these two ions influences the comparative destructiveness of each ion. The OH^- ion is much larger than the H^+ and therefore will be restricted to reacting with the exposed external surfaces of the minerals, which in the case of smectite would be the siliceous basal surfaces, whereas, the H^+ due to its smaller size could react with the enclosed Al octahedral sheet and dissolve Al, while leaving the siliceous framework intact. This could explain the low solubility of the smectitic soil in the base equilibration. This reasoning also helps to explain why similar amounts of Al and Si were released by the base equilibration of the smectitic soil (Fig. 1.5b), as less Al was available for dissolution, than compared with the other soil types which contained less 2:1 layer silicates.

The reason for the kaolinitic soil (Fig. 1.5) releasing similar amounts of Al and Si in both the acid and base equilibrations could be due to the fact that kaolinite is a 1:1 layer silicate with the Al octahedral sheet being exposed equally as much as the Si tetrahedral sheet, thus both the H^+ and OH^- groups would have equal opportunities for dissolving Al and Si. Table 1.2 provides a summary of the Al, Si and Fe results at 35 days.

Table 1.2 Comparison of the dissolution of Al, Si and Fe (expressed per unit mass of soil) at 35 days during the acid- and base-equilibration of the soils.

Soil treatment	**Al**	**Si**	**Fe**
	----------mmol.kg soil^{-1}----------		
Organic - acid	165	61.4	23.5
Organic - base	63.3	22.5	17.0
Smectitic - acid	124	58.5	6.6
Smectitic - base	16.3	15.9	<0.2
Sesquioxidic - acid	285	49.6	<0.2
Sesquioxidic - base	117	8.4	<0.2
Kaolinitic - acid	75.2	30.0	10.2
Kaolinitic - base	82.3	20.4	0.6

In the acid equilibrations, the sesquioxidic soil showed the greatest release of Al, with about double the amount being release compared to the other soil types (Table 1.2). This is most probably due to its high clay (83%) and gibbsite content (Table 1.1).

The most Fe was released from the organic soil (Table 1.2). It is possible that the organic matter complexed any released Fe during dissolution, thus allowing for the release of more Fe into solution, than compared to the other soils.

Another interesting observation is the inflection in the curve of the base treatments after a period of one week of equilibration. This is particularly evident in the organic and sesquioxidic soils. Even after these equilibrations were repeated the same phenomenon appeared (Appendix 1 – Fig. A1.1 – A1.4). This could possibly indicate a step-wise dissolution occurring at the high pH. Another explanation could be the precipitation of an Al and Si hydroxide under the specific pH conditions due to the supersaturation of the solution with regards to Al and Si, due to continuous dissolution. At this point the high concentrations of Al and Si in solution force the reaction in the direction of the precipitation of the product which would account for the abrupt lowering of the Al and Si in solution. However, dissolution continues with the remaining unreacted soil components and the pH also continues to decrease as a result of the buffering, so the conditions in solution again become unfavourable for the precipitation of the specific compound and so the Al and Si concentrations once again increase in solution. It is unknown what this intermediary reaction product might be, and would require further investigation and more extensive analysis of the solution.

It can also be seen in the base equilibration the organic soil (Fig. 1.3b), that towards the end of the equilibration period there is a decrease in the amount of Al, Si and Fe in solution. This trend can also be observed to a lesser degree in the sesquioxidic soil's base equilibration (Fig. 1.5b). This corresponds with the pH data shown in Fig. 1.7, recorded over the 5 week equilibration period (Tabulated pH values are given in Appendix 1, Table A1.1). The greatest change in pH during base equilibration was observed in the organic soil (Fig 1.7b), so this could indicate the precipitation of Al, Si and Fe hydroxides as the pH decreases.

In the acid equilibration it can be seen that the sesquioxidic soil showed the greatest change in pH over time, and this corresponds to the greater dissolution of Al and Si (Fig. 1.7a). The organic soil showed the greatest change in pH over time during the base equilibration, then the sesquioxidic, smectitic and kaolinitic soil. There appears to be an inflection in the sesquioxidic curve, but it could be due to pH measurement error. However, this also corresponds with the inflection observed in the Al and Si dissolution at the same period. This supports the explanation above, with regards to the formation of a temporary precipitate due to supersaturation. When precipitation occurs there should be a sudden decrease in the pH due to the consumption of hydroxyl groups, which is exactly what is observed. The pH however then increases again, as does the Al and Si concentrations in

solution at a period of 2 weeks. This could be as result of the dissolution of the product which temporarily formed, but became unstable due to the sudden lowering of the pH of the solution.

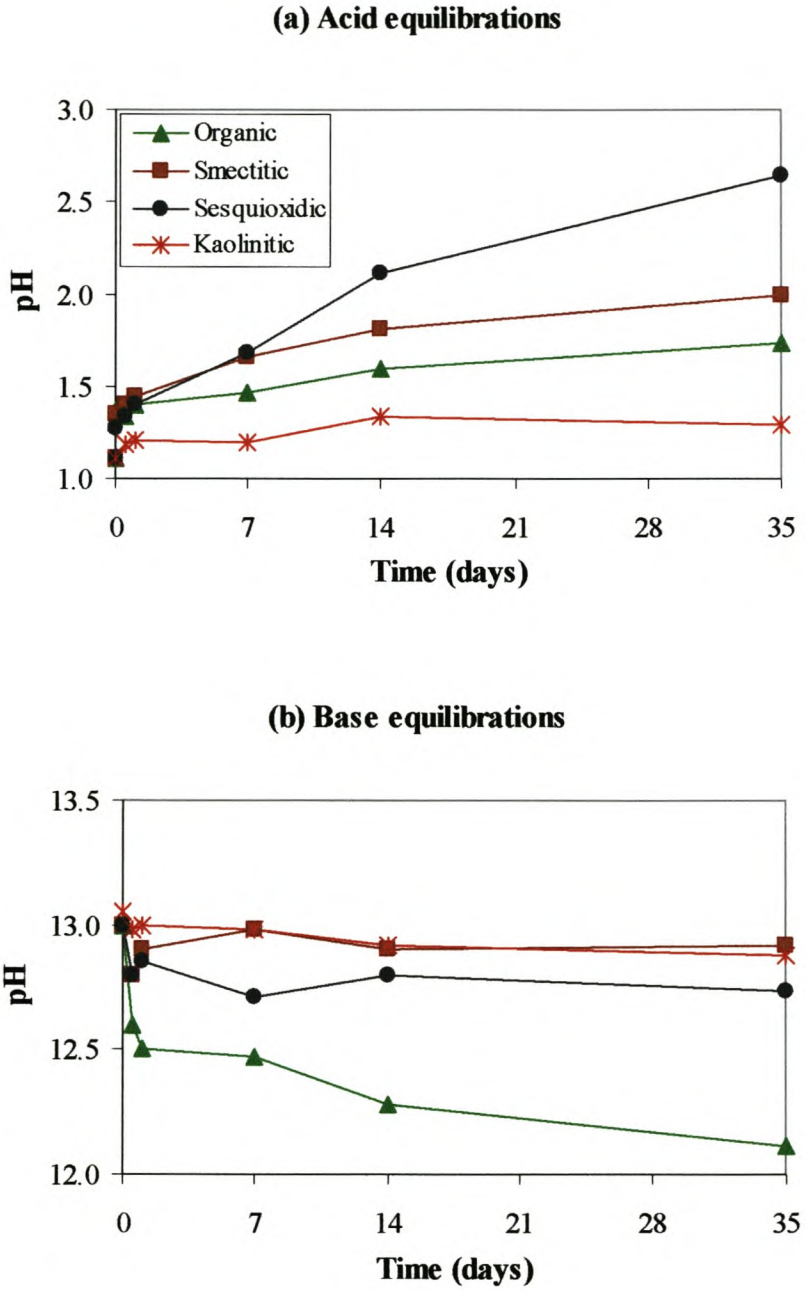


Figure 1.7 Change in pH during (a) acid and (b) base equilibration of the soils over the 5 week period.

It is understandable that the organic soil would be the most well buffered soil at the high pH due to the hydrolysis of the large amount of organic matter present in the soil. The smectitic

soil showed little change in pH in the base equilibration and this corresponds with its low release of Al and Si (Fig.1.4b).

The dissolved Al/Si molar ratio of acid- and base-equilibration of the soils over the 5-week period is shown in Fig. 1.8 and 1.9.

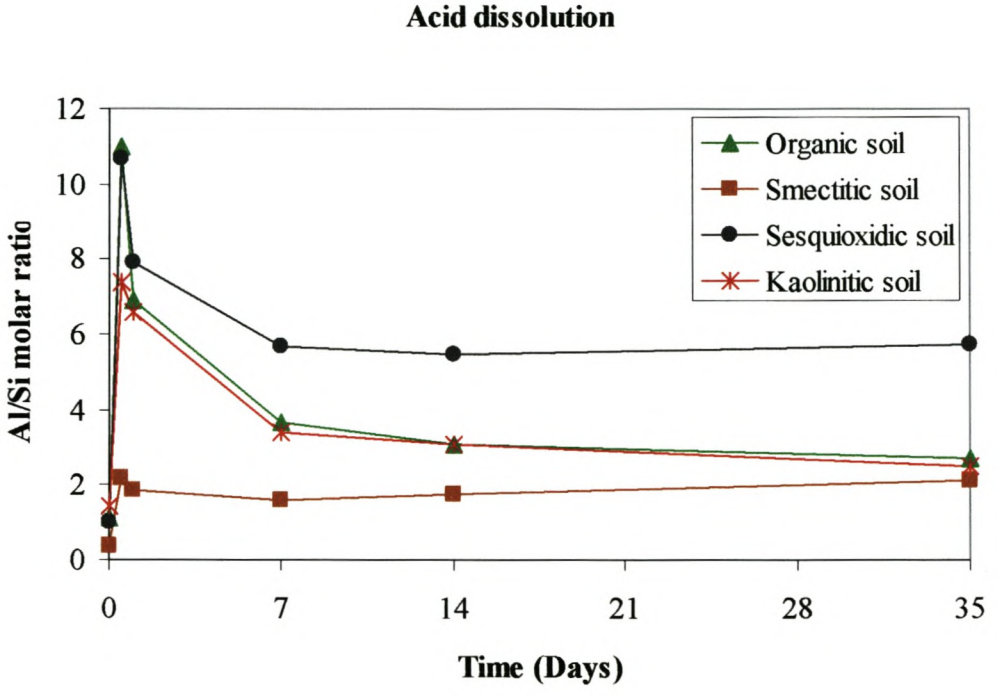


Figure 1.8 Dissolved Al/Si molar ratio of the acid dissolution of the soils over the 5 week period.

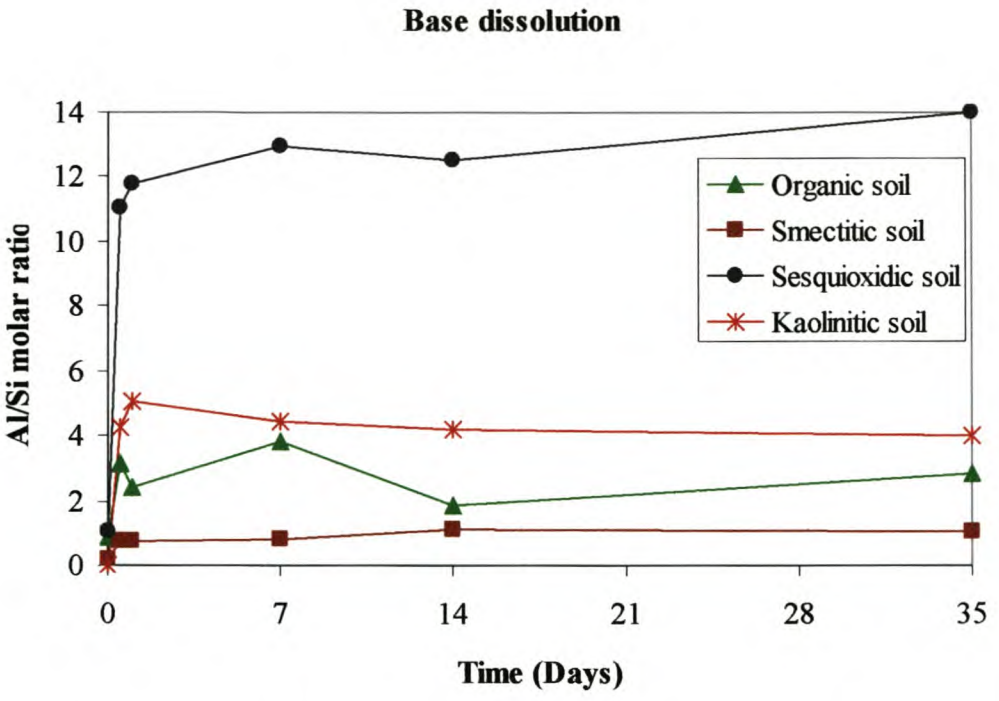


Figure 1.9 Dissolved Al/Si ratio of the base dissolution of the soils over the 5 week period.

The dissolved Al/Si molar ratios of the kaolinitic and organic soils were almost identical during the acid dissolution (Fig. 1.8). This could be attributed to the fact that both soils' clay fractions are dominated by kaolinite (Table 1.1). The sesquioxidic soil had the highest Al/Si ratios during both the acid and base dissolution, and this is explicable because it is gibbsite dominated, and thus has a low Si content. During acid dissolution the Al/Si ratio is initially high and then declines after a period of about 7 days, whereas during base dissolution there are only small changes in the ratio over time. This means that Al is initially released more easily into solution than Si during the acid dissolution, but eventually the ratio becomes smaller and remains stable. This could indicate that first octahedral sites on the clay minerals are more accessible to acid attack by HCl than the tetrahedral sites. These results are in contrast to the results of Yeoh and Oades (1981a), where they found that phosphoric acid resulted in the preferential dissolution of the tetrahedral silica sheets of illite and bentonite, than compared to the octahedral sheet. They found that equimolar amounts of Al and Si were released from kaolinite, showing that the tetrahedral and octahedral sheets were equally susceptible to acid dissolution. In their study, however, they were investigating the dissolution of relatively pure clay minerals, and their concentrations of acid were higher.

The dissolution Al/Si ratios of the base equilibrated soils tend to stay the same, with only minor fluctuations during the equilibration period (Fig. 1.9). The sesquioxidic and organic soils once again show inflections, similarly observed in the Al and Si dissolution data at a period of 1 week. These inflections show that at that point the Al in solution was higher than Si than compared to the other dissolution conditions. This could mean that the product that is being formed possibly contains much Si.

1.4 Conclusions

As was expected, the four contrasting soil types reacted differently to the acid and base equilibrations at extremely acid or alkaline conditions. The results of Al, Si and Fe release during the equilibrations can be summarised as follows:

- Acid Al release: sesquioxidic >> organic > smectitic > kaolinitic
- Base Al release: sesquioxidic > organic > kaolinitic > smectitic
- Acid Si release: smectitic ≈ organic > sesquioxidic > kaolinitic
- Base Si release: organic > kaolinitic > smectitic > sesquioxidic
- Acid Fe release: organic >> kaolinitic > smectitic > sesquioxidic
- Base Fe release: organic > kaolinitic ≈ sesquioxidic ≈ smectitic

In general the acid equilibration resulted in a greater release of Al and Si, than the base equilibration, except in the case of the kaolinitic soil (Fig. 1.5), where similar amounts of Al and Si were released. This could be ascribed to the difference in destructiveness of the H^+ and OH^- ions, based on their ionic radii, and their ability to access interlayer positions in 2:1 layer silicates.

Al was released in much greater quantities than Si or Fe into solution during the both the acid and base equilibrations. The only exception was the base treatment of the smectitic soil, where similar amounts of Al and Si were released. This could also be attributed to the inaccessibility of the octahedral sheet to OH^- attack in 2:1 layer silicates, due to its large ionic size.

Inflections were clearly observed in the base dissolution of the sesquioxidic and organic soils, at a period of 1 week. This could be attributed to step-wise dissolution. However, it is

possible that this is a result of supersaturation of the solutions at a specific pH, which results in the forced precipitation of a mineral phase, which later then becomes as unstable as the pH decreases. The pH data seem to support this observation.

The dissolved Al/Si ratio of the acid equilibrated soils was initially high and then after a period of about 7 days the ratio decreased and remained stable. This suggests that octahedral positions on the clay minerals are initially more accessible to acid attack, and after dissolution has progressed the tetrahedral positions also undergo more dissolution. The dissolved Al/Si ratio of the base equilibrated samples tended to remain the same throughout the equilibration period. The Al/Si was greater than 2 for the majority of the samples, which shows the preferential dissolution of Al over Si during extreme pH conditions.

It was concluded that a period of one or two weeks could be considered enough time for the significant release of Al and Si into solution for precipitation of new solids, for the acid and base priming treatments.

Chapter 2

2 THE EFFECT OF ACID/BASE PRIMING ON SORPTIVE PROPERTIES OF SOIL

2.1 Introduction

The process of acid- or base-priming can be defined as subjecting the soil to extremely high or low pH conditions for a period of time to allow dissolution to take place, and then re-adjusting to a neutral pH, approximately the same as that of the soil's original pH. Equilibration at the extreme pH allows for the release of Al, Si and Fe, as demonstrated in the previous chapter, which are then later fully precipitated during the neutralisation step. In theory one can generate new more reactive surfaces by this acid or base priming, with the primary aim being to make soils more adsorptive of inorganic contaminants, with possible environmental remediation applications.

Acid and base priming was investigated on the four soils from Chapter 1 (organic; smectitic; sesquioxidic; kaolinitic), as a follow up to the dissolution studies carried out on these soils in the previous chapter. Since I had attained quite a good picture of what was happening to these soils during acid or base dissolution, I hoped that this could be correlated with change in the properties of these soils after being primed. The first chemical characteristic that was investigated on the primed and un-primed soils was the metal cation sorption capacity, using Cd(II) and Cu(II). The anion sorption properties were then investigated using PO_4^{3-}. BET specific surface area determinations were carried on two of the soils to see whether there was a change in surface area due to these treatments, as was initially anticipated. Finally surface charge determinations were performed on all the soils, which gave a good indication of the change in the buffer capacity of these soils due to the acid- and base-priming. The following review looks at some of the principles of Al, Fe and Si oxide and hydroxide formation in soils.

Non-crystalline aluminosilicates (allophanes), oxides and hydroxides of Fe and Al provide surface sites for the chemisorption of a wide range of metals and ligands (McBride, 1994). Al and Fe hydroxides and oxyhydroxides occur as weathering products in acid soils.

Aluminium and silica co-precipitate in the pH range of 4 to 11 (McBride, 1994). The co-ordination number of Al in such structures has important implications for charge development (Wilson *et al.*, 1986). Organic matter inhibits precipitation by complexing with metal cations in acid solution, leading at most to the precipitation of poorly-ordered precipitates (Lahodny-Šarc and Dragčević, 1981; Violante and Violante, 1980). However, amorphous precipitates have a larger, more reactive surface area and thus possess a larger adsorptive capacity (Garcia-Sanchez *et al.*, 2002). Wada and Wada (1980) investigated the formation and composition of hydroxyaluminium and hydroxyaluminosilicate (HAS) ions. They found that $Si(OH)_4$ reacts only with hydrolysed polymers of Al ions, and that the formation of HAS ions forms primarily as a condensation reaction between the hydroxyl groups.

Bowden *et al.* (1980) reviewed adsorption and charging phenomena in variable charge soils. Early work on variable charge soils was carried out by Mattson (1931), Schofield (1949) and Sumner (1963). The amount of variable charge which develops in soils largely depends on the amount of active Fe and Al in soils (Parfitt, 1980). Fey and Le Roux (1975) examined the phenomenon of pH-dependent exchange charge in a variety of sesquioxidic colloidal materials. Kinniburgh *et al.* (1976) investigated the adsorption of divalent metal cations on hydrous oxide gels of Al and Fe. They stated that these gels have the ability to adsorb divalent cations specifically. They found that significant adsorption occurred even when the extent of cation hydrolysis was much less than 1%, and that adsorption occurred at a lower pH than for hydroxide precipitation.

Veerhoff and Brümmer (1993) investigated the extreme acidification of forest soils in Germany and found that the acid weathering products were amorphous aluminosilicate compounds which occurred as silicic coatings on surface of soil aggregates. They reported that these coatings reduced the CEC of soils as they smothered the existing mineral surfaces. Robert and Terce (1987) reviewed the literature regarding the effect that Al gels and coatings have on the chemical properties of clay minerals. They concluded that a consequence of the presence of coatings is that they confer specific anion and cation adsorption properties to soil clay minerals. Schulthess and Huang (1990) investigated the adsorption of heavy metals by Al and Si oxides on the surfaces of clay minerals. They stated that the affinity of metal ions towards Si and Al oxide coatings on clay surfaces is dependant on the pH of the medium, the Lewis acid strength and the type of surface site. They also

concluded that the magnitude of the permanent charge of 2:1 clay minerals may be due to adsorption on amorphous Si-oxide sites that could induce ion-exchange reactions at much lower pH values than previously assumed. McBride (1994) gives a clear explanation of sorption of metal cations and anions on aluminosilicates and oxides in the soil. Non-crystalline aluminosilicates, oxides and hydroxides of Fe, Al and Mn, and the edges of layer silicate clays provide sites for the chemisorption of metal cations and anions. All these minerals possess a similar type of adsorptive site to the soil solution, namely a valence-unsatisfied OH^- or H_2O ligand bound to a metal ion (e.g. Fe^{3+}, Al^{3+}). Sorption of metal cations takes place with the release of H^+, whereas sorption of anions takes place with the consumption of H^+. McBride (1994) also discussed the specific adsorption of cations and anions simultaneously through what is known as ternary complexes. In this case a metal cation can form a link with an anion and hydroxyl group of a variable charge mineral surface. An anion can also provide a link for a metal cation.

Schneidegger and Sparks (1996) critically reviewed sorption-desorption mechanisms that occur at the soil mineral/water interface. It was concluded that the present understanding of sorption processes is still in its infancy and that there is still a lot of detailed study that need to be carried out, as no single technique can elucidate the exact mechanisms involved. Ford *et al.* (2001) reviewed the latest discoveries in sorption/precipitation mechanisms on soil mineral surfaces. The review provides a critical synopsis of all the surface complexation models that are currently employed.

Yeoh and Oades (1981a & b) acidified clay minerals and soil for a period of time using phosphoric acid and nitric acid. When the reaction products from the acidification with phosphoric acid were precipitated in the presence of clay, they were shown to exist as an aluminium phosphate containing amorphous silica. They concluded that phosphoric acid treatment of soil should improve the aggregation of soils by supplying interstitial cements of aluminium phosphate and silica. Garrido *et al.* (2003) investigated the use of gypsum-like by-products to counter soil acidity. They found that the polymerization of exchangeable Al in acid soils was promoted by the addition of these industrial by-products, and that the adsorption of these Al polymers was particularly favourable in horizons with a higher content of clay and variable-charge clay minerals.

The concept of acid or base priming is in some ways similar to the research conducted on interlayer hydroxyaluminium- and hydroxyaluminosilicate-montmorillonite and vermiculite

complexes (Rich, 1960; Barnhisel, 1977), specifically focusing on the effect these complexes have on the surface charge characteristics (Inoue and Satoh, 1993; Sakurai and Huang, 1998; Janssen *et al.*, 2003a) and metal cation (Harsh, and Doner, 1984; Lothenbach *et al.,* 1997 & 1998; Saha *et al.,* 2001 & 2002; Janssen *et al.*, 2003b) and anion (Saha *et al.,* 1998) adsorptive properties of soils. In these studies the hydroxyaluminium (HyA) and hydroxyaluminosilicate (HAS) complexes are synthesised by titrating an Al salt (e.g. $AlCl_3$) and orthosilicic acid (in the case of the hydroxyaluminosilicate), with NaOH to achieve an Al/OH molar ratio of 2.0 - 2.5. The complexes are then aged and reacted with montmorillonite. The complexes form partially neutralised hydroxide layers at the mineral surface and in the interlayer position. It was found that these complexes brought about a significant change in the chemical properties of the montmorillonite clay, resulting in a reduction in the permanent negative charge and a substantial increase in pH-dependant negative charge (Inoue and Satoh, 1993; Lothenbach *et al.*, 1998; Saha *et al.*, 2001). Consequently, these surface complexes have been found to significantly increase the specific adsorption of metal cations such as Cu (Harsh and Doner, 1984; Lothenbach *et al.,* 1997), Cd, Zn and Pb (Lotenbach *et al.,* 1997; Saha *et al.,* 2001). Lothenbach *et a*l. (1997) even suggested that these Al based binding agents could be used for the gentle remediation of soils contaminated with Ni, Cu, Zn or Cd, as these metals were immobilised by HyA complexes.

2.2 Materials and methods

2.2.1 Acid/base priming of the soils

The four soils described in Chapter 1 were primed for the adsorption studies by acid or base equilibration at an extreme pH and then titrated back to their original pH. This treatment involved taking 40g of soil and suspending it in 400 ml 0.1 M HCl or KOH for a period of two weeks, while shaking gently. After the acid or base equilibration, the samples were titrated back to their original pH prior to the acid or base treatment using 1 M HCl or KOH, with 0.05 ml additions at 30s intervals. These titrations were carried out using automatic titration equipment (Mettler DL21) and it took about 6 hours to complete a titration. The change in pH was continually recorded as the acid or base was added using a computer. The titrated soils were then centrifuged to separate the soil from the soil solution and washed at

least three times using a 1:1 ethanol and distilled water mixture to prevent dispersion of the clay. The samples were washed until the electrical conductivity of wash water was approximately the same as that of the untreated soil sample in a 1:10 suspension of distilled water (Appendix 2, Table A2.1). The washed soil samples were then dried at 50° C until completely dry, and then lightly ground in a mortar. An untreated control sample of each soil type was also dried at 50° C for about 48 hours and then ground.

2.2.2 Cadmium and copper sorption

The three soil treatments (acid-primed; base-primed; untreated) were compared in terms of their effect on sorption of Cd(II) and Cu(II). All four soils were used for Cd sorption, whereas, only the smectitic and sesquioxidic soils were used in the Cu sorption study. Sorption was effected using 1g of soil suspended in 25 ml $CdCl_2.H_2O$ or $CuCl_2.2H_2O$ solution. Five different Cd concentrations were used, ranging between 500–12500 $mg.kg^{-1}$ and four Cu concentrations ranging between 2500-25000 $mg.kg^{-1}$. Each treatment was performed in duplicate (Appendix 2, Table A2.1). The samples were shaken for 24 hours in sealed polyethylene bottles, and then centrifuged and filtered using Whatman no. 640d filter paper. The Cd in solution was determined using flame atomic adsorption spectroscopy (AAS) (Perkin Elmer 3100), while Cu was determined using an ICP-Mass Spectrometer (ICP-MS) (Perkin-Elmer Sciex Elan 6000) equipped with a quadrupole mass filter, a Scott type spray chamber and a Meinhard type nebulizer. External calibration was used on the ICP-MS but rhodium was added to the samples and standards as an internal standard for drift correction. Reproducibility of the AAS and ICP determinations are shown in Appendix 2, Tables A2.2 – A2.3.

The Cd 12500 $mg.kg^{-1}$ treated samples were taken after being separated from the solution and then shaken with 25 ml 1 M NH_4NO_3 for 24 h to determine the percentage immobilized Cd (Usman *et al.*, 2002). The samples were then centrifuged and filtered, and the Cd concentration in the filtrate was determined using flame AAS. Reproducibility of the AAS determinations is shown in Appendix 2, A2.4.

2.2.3 Phosphate sorption

Phosphate sorption studies were carried out on all four of the acid-, base-primed and untreated soils. The method used was based on that of Rowell (1993). The procedure employed 0.5g soil sample and suspended it in 12.5 ml of KH_2PO_4 solution. A range of 5 different phosphate concentrations was tested, as well as a control sample. They ranged between 250 $mg.kg^{-1}$ soil and 1500 $mg.kg^{-1}$ soil, depending on the soil type. The samples were shaken for 24 h in sealed polyethylene bottles and then filtered using Whatman no. 2 filter paper. The phosphate content in the filtrate was determined colorimetrically using the ammonium molybdate method (Rowell, 1993) Up to 5ml of sample was pipetted into a 50 ml volumetric flask, 8ml of ascorbic acid solution (1.5g ascorbic acid in 100 ml distilled water) and 8 ml of the ammonium molybdate solution. The solutions were allowed to stand for 30 min before reading absorbance at 880 nm with a Pharmacia Ultrospec III spectrophotometer.

2.2.4 BET specific surface area

The specific surface area (SSA) of the sesquioxidic and kaolinitic acid/base primed and control samples was determined using the Brunauer-Emmett-Teller (BET) method (Sparks, 1995). The samples were dried in the oven at 50° C for 24 h prior to the determination. The SSA was determined using N_2 gas on a Micromeritics Accelerated Surface Area and Porosimetry 2010 system. Degassing was performed at 50° C so as to avoid crystallising any potentially amorphous metal hydrous-oxide precipitates (Kaiser *et al.*, 2003) that may have been formed during the neutralisation step of the acid or base priming.

2.2.5 Surface charge

The surface charge of the acid-, base-primed and untreated soils, was determined using a similar approach to that described by Hunter (1981). Three solutions of KCl with concentrations of 1.00, 0.10 and 0.01 M were used as background solutions during the determination. The procedure involved taking 0.5g soil and suspending it in 50 ml KCl solution in polyethylene bottles, to which an amount (0.02 - 0.05 ml) of standardised 1 M NaOH or 1 M HCl was added to adjust the pH within an intended range of pH 3 – 10. The acid or base was dispensed using a Metrohm 702 SM Titrino titrator. The suspensions were

shaken for 20 hours in the sealed polyethylene bottles, and then allowed to settle for 30 min before the pH was measured (Beckman Φ32 pH meter).

2.3 Results and discussion

2.3.1 Acid/base priming of soils

The titration curves obtained during the neutralisation step of the acid- and base-primed soils, using 1 M KOH and 1 M HCl, are shown in Fig. 2.1 & 2.2, respectively. Table 2.1 shows the Al and Si dissolution data (Chapter 1) of the soils, at 2 weeks, and the approximate length of the 2nd buffer range of the titration curves of the acid-primed soils. Table 2.2 shows pH values measured in solution during the acid and base priming treatments.

The acid-treated soils (Fig. 2.1) clearly show different buffer ranges. The first buffer range (pH 1 - 3.5) is due to the neutralisation of the any excess acid present. This is confirmed by noting that the higher the starting pH (Table 2.2) of the titration, the smaller (in mmol OH^- added.kg^{-1} soil) the first buffer range. This is particularly evident in the kaolinitic sample, which had the least Al release during equilibration studies (Table 2.1), and also showed the least change in pH during the equilibration period (Fig. 1.7b). The second buffer range (pH 3.5 - 5) most probably indicates the precipitation of Al that was released during the acid equilibration, as hydroxides. This statement can be made based on the Al release data for the particular soil (from Chapter 1) and comparing it to the approximate length (in mmol OH^- added.kg^{-1} soil) of the second buffer range (Table 2.1). These distinct buffer ranges were also noted by Schwertmann and Jackson (1964), who attributed the second buffer range to the precipitation of exchangeable $Al(OH_2)_6^{3+}$.The base-treated soils' titration curves (Fig 2.2) are not that distinctive, yet they also seem to indicate the presence a second buffer range in the pH range 9 - 11. It is possible that this is due to the formation of K-allophane or K-silicate. As CO_2 was not excluded from these experiments it may also be due to the involvement of carbonate equilibria.

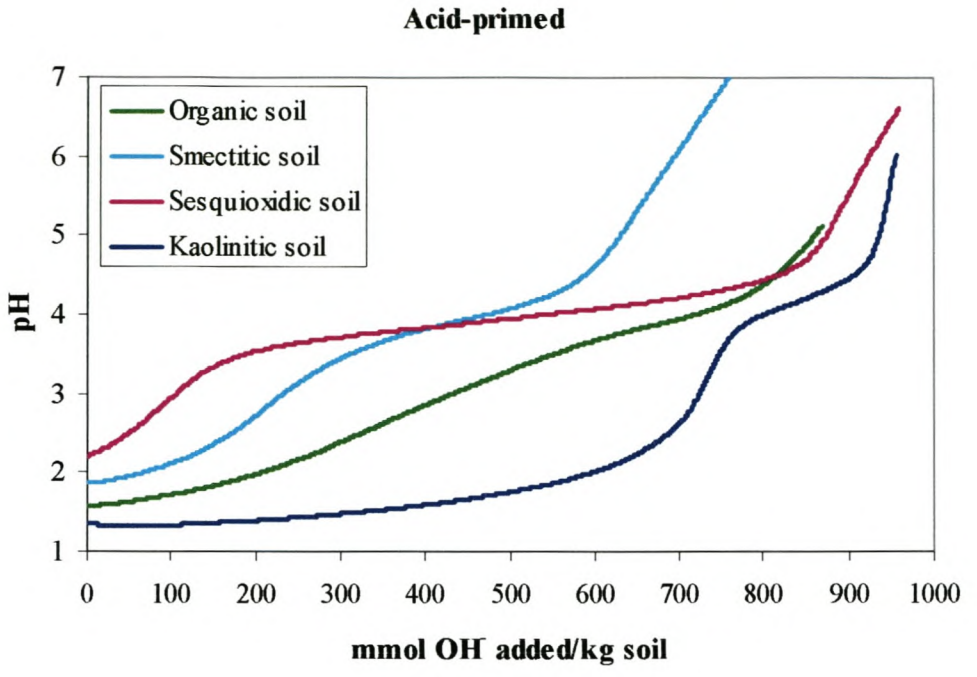


Figure 2.1 Titration curves of the acid-primed soils with KOH.

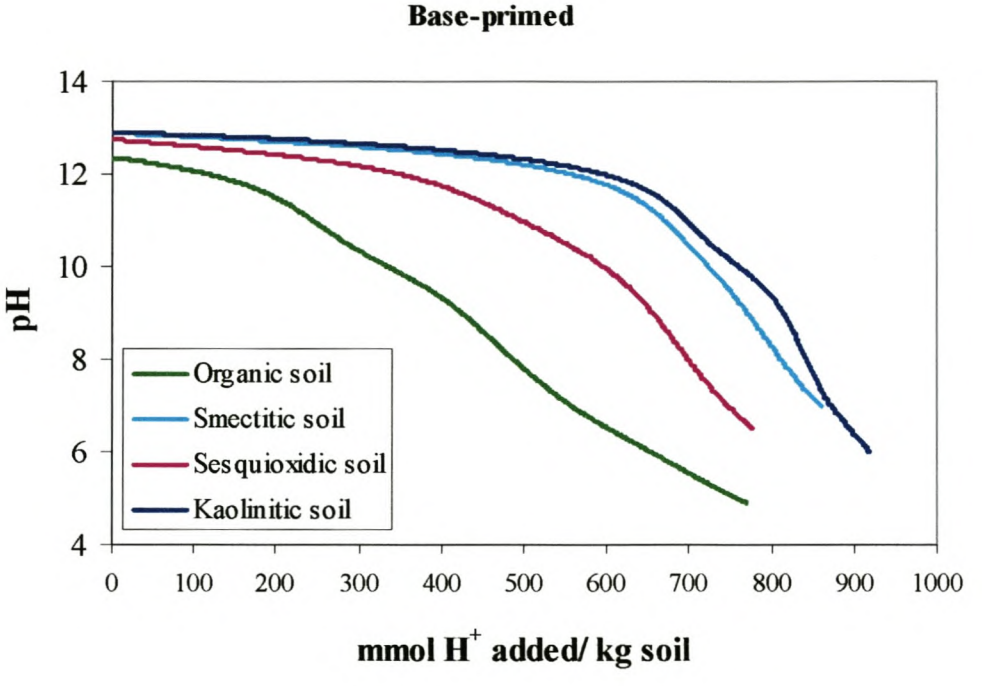


Figure 2.2 Titration curves of the base-primed soils with HCl.

Table 2.1 Comparison of the Al and Si dissolution data (Chapter 1) of the soils, at 2 weeks, with the approximate length of the 2nd buffer range of the titration curves of the acid-primed soils

Soil	Al released at 2 weeks (mmol.kg^{-1} soil)	Si released at 2 weeks (mmol.kg^{-1} soil)	Molar Al/Si ratio -	Approximate length of 2nd buffer range (mmol OH^-.kg^{-1} soil)
Acid dissolution				
Organic	134	34.9	3.1	245
Smectitic	107	66.1	1.7	299
Sesquioxidic	581	43.4	5.5	681
Kaolinitic	102	16.1	3.1	167
Base dissolution				
Organic	93.0	50.0	1.9	-
Smectitic	16.4	14.0	1.1	-
Sesquioxidic	119	9.5	12.6	-
Kaolinitic	77.6	18.4	4.2	-

Table 2.2 Soil suspension pH during and after the acid and base priming treatment.

Soil	pH initial	pH after 1 week	pH after 2 weeks	pH adjusted	pH after drying (1:25 H_2O)
Acid-primed					
Organic	1.1	1.5	1.6	5.0	5.6
Smectitic	1.1	1.6	1.9	7.0	7.0
Sesquioxidic	1.1	1.8	2.2	6.5	6.7
Kaolinitic	1.1	1.2	1.4	6.0	6.4
Base-primed					
Organic	13.0	12.6	12.3	5.0	6.5
Smectitic	13.0	12.9	12.3	7.0	9.0
Sesquioxidic	13.0	12.8	12.7	6.5	8.4
Kaolinitic	13.0	12.9	12.9	6.0	7.0

2.3.2 Cadmium and copper sorption

Sorption curves for the four soils are shown in relation to acid and base treatment, for Cd (Fig. 2.3 & 2.4), and for the smectitic and kaolinitic soil for Cu (Fig. 2.6).

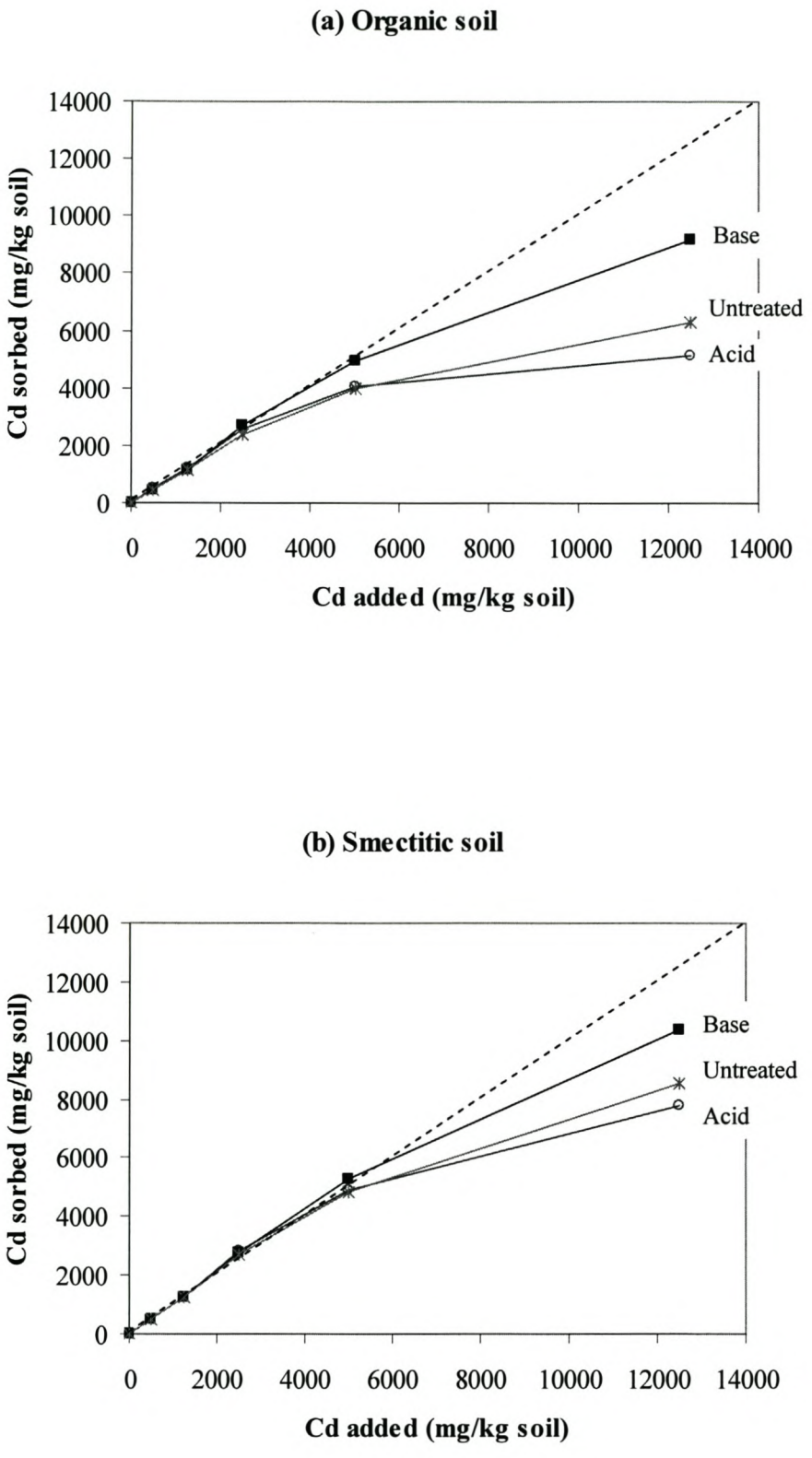


Figure 2.3 Cd sorption relative to the amount of Cd added to acid-, base-primed or untreated soils: (a) organic and (b) smectitic soil (broken line represents complete sorption).

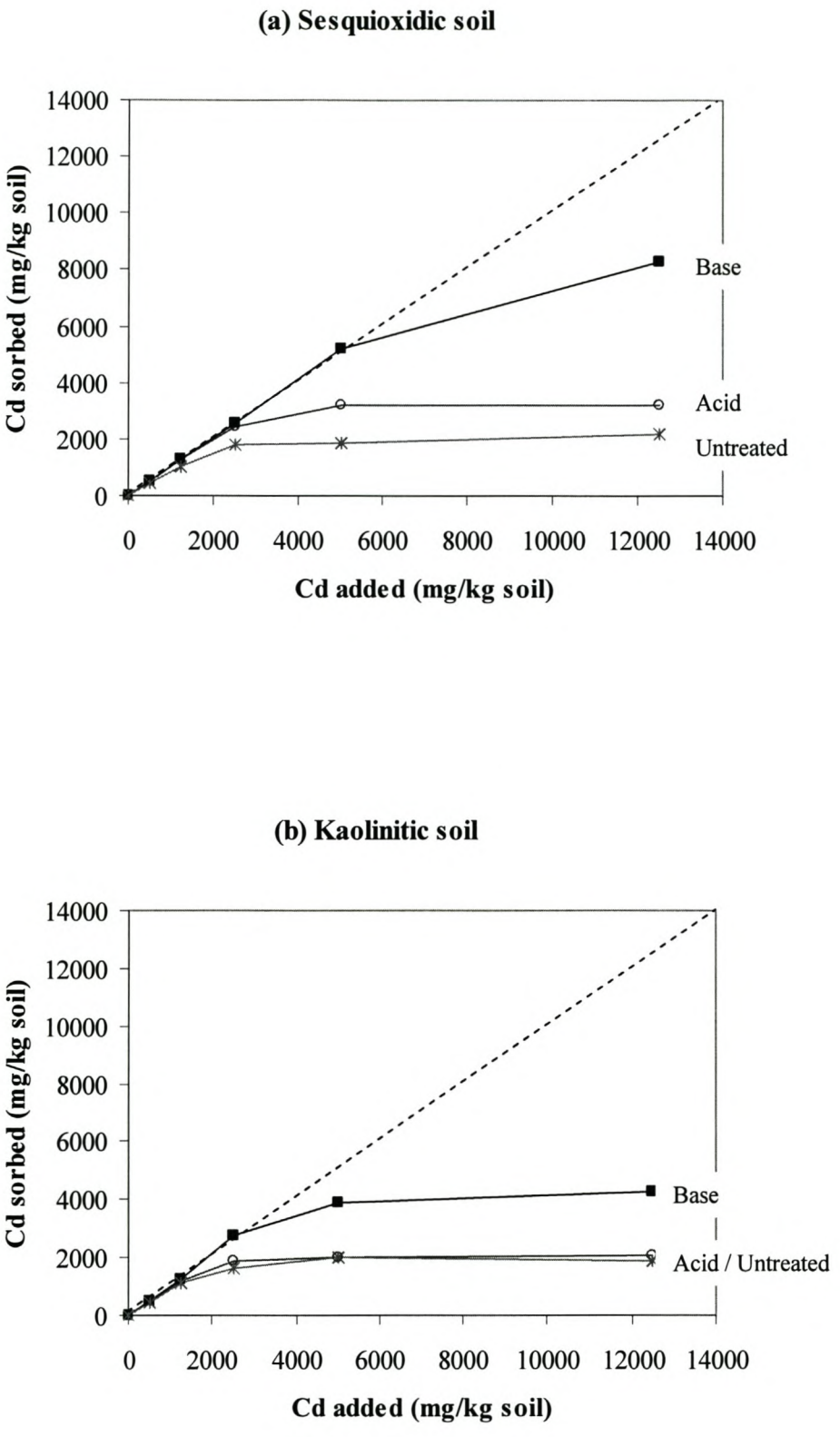


Figure 2.4 Cd sorption relative to the amount of Cd added to acid-, base-primed or untreated soils: (a) sesquioxidic and (b) kaolinitic soil (broken line represents complete sorption).

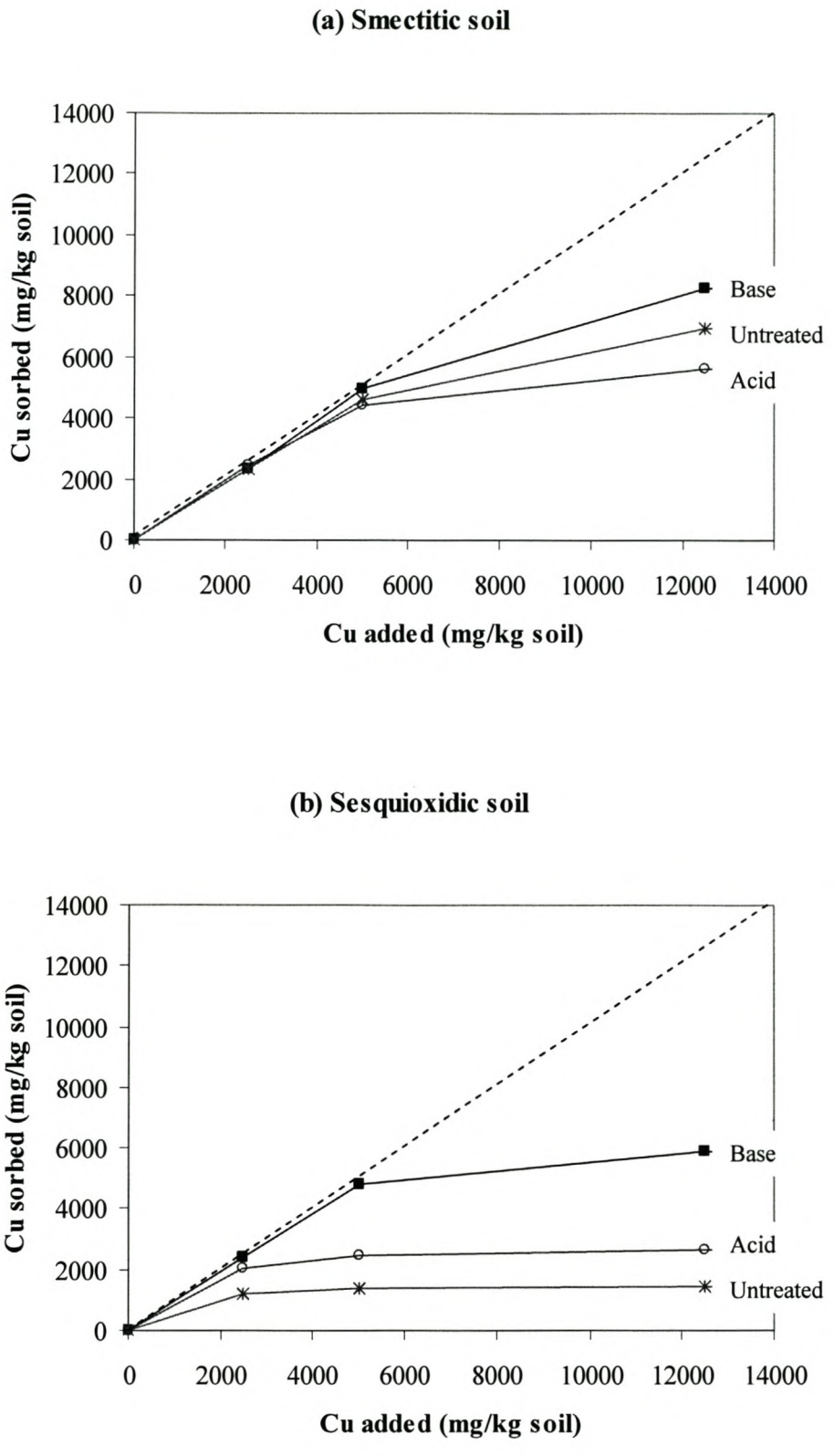


Figure 2.5 Cu sorption relative to the amount of Cu added to acid-, base-primed or untreated soils: (a) smectitic and (b) sesquioxidic soil (broken line represents complete sorption).

Base priming resulted in increased Cd sorption in all four soils, whereas the acid treatment had little or a negative effect except in the case of the sesquioxidic sample (Fig. 2.4). The greatest relative increase (54.0 mmol.kg^{-1} soil) in Cd sorption due to the base priming was observed in the sesquioxidic soil (Fig. 2.4b). The second largest relative increase (21.4 mmol.kg^{-1} soil) due to the base treatment was in the kaolinitic soil, where the adsorption of Cd was effectively doubled (Fig 2.4b). Table 2.3 provides a summary of the observed increases and decreases in adsorption of Cd and Cu.

Table 2.3 Summary of the Cd and Cu sorption study results for the 12500 mg.kg^{-1} soil treatment, comparing the increase or decrease in sorption from the untreated soil.

Treatment	Cd sorbed (mmol.kg^{-1} soil)	Fraction Cd sorbed of total added	Incr. (⬆) or decr. (⬇) (mmol.kg^{-1} soil)	Cu sorbed (mmol.kg^{-1} soil)	Fraction Cu sorbed of total added	Incr. (⬆) or decr. (⬇) (mmol.kg^{-1} soil)
Organic						
Untreated	55.9	0.48	-	-	-	-
Acid-primed	45.8	0.40	⬇10.1	-	-	-
Base-primed	81.8	0.70	⬆25.8	-	-	-
Smectitic						
Untreated	76.0	0.65	-	109.5	0.56	-
Acid-primed	69.2	0.60	⬇ 6.8	88.1	0.45	⬇21.4
Base-primed	92.4	0.80	⬆16.4	130.3	0.66	⬆20.8
Sesquioxidic						
Untreated	19.5	0.17	-	22.3	0.11	-
Acid-primed	28.6	0.25	⬆ 9.1	41.4	0.21	⬆18.8
Base-primed	73.5	0.64	⬆54.0	93.0	0.47	⬆70.7
Kaolinitic						
Untreated	16.9	0.15	-	-	-	-
Acid-primed	18.5	0.16	⬆ 1.6	-	-	-
Base-primed	38.3	0.33	⬆21.4	-	-	-

The Cu sorption study showed similar results to that of the Cd sorption study, whereby base-priming resulted in a significant increase in the metal cation sorption of the sesquioxidic soil, and to a lesser extent in the smectitic soil (Fig. 2.5). Similarly, the acid treatment resulted in an increase in Cu sorption in the sesquioxidic sample only.

The increase in the sorption due to base-priming can be related to the amount of Al released as observed in the equilibration studies. The comparison of the amount of Al released during the base equilibration was as follows: sesquioxidic >> organic > kaolinitic > smectitic

(Table 2.4). This is reflected by the Cd sorption curves, with the soils showing an increase in Cd sorption in a similar order, sesquioxidic >> organic > kaolinitic > smectitic, as the release of Al. Thus it can be hypothesised that the greater the susceptibility of a soil to base dissolution the greater the increase in metal cation sorption due to base priming. As discussed in the previous chapter, the amount and type of clay minerals which are dominant in a soil determine the susceptibility of the soil to dissolution.

Table 2.4 Comparison of Al released during base dissolution (at 2 weeks) with amount of Cd sorbed

Soil	**Al released (mmol.kg^{-1} soil)**	**Cd sorbed (mmol.kg^{-1} soil)**
Organic	93.0	25.8
Smectitic	15.4	16.8
Sesquioxidic	119.0	54.0
Kaolinitic	77.6	21.4

To explain the phenomenon of base priming increasing the metal cation sorption and acid priming decreasing or having little effect on it, except in the sesquioxidic sample, one has to take into account the nature of the precipitates that would be formed from the acid or base dissolution processes. It can be hypothesised that the precipitates that form from the reaction products of basic dissolution would be more siliceous, as Si is most soluble at pH values above 9 as the silicate anion, $Si(OH)_3^-$. It can be proposed that due to the fact that at a high pH the dissolved Al would be in the tetrahedral form so the HAS precipitates that would form during reprecipitation would most likely have some isomorphous substitution of Al for Si and thus would thus have a permanent negative charge to some extent. This was observed by Yokoyam *et al.* (2002), when they synthesised an amorphous aluminosilicate on the surface of a crystalline Al hydroxide absorbent. The aluminosilicate was synthesised by adding a solution of silicic acid at a high pH (7 -10) to the Al absorbent. They found that the amorphous aluminosilicate had a strong permanent negative charge, and they attributed this to isomorphous substitution of Al for Si, specifically as their NMR investigation showed that the Al(6) had been rapidly converted to Al(4) when the monosilicic acid was adsorbed on the Al hydroxide. The negative charge generated by the amorphous aluminosilicate precipitates would explain the increase in metal cation adsorption observed in the base primed samples.

On the other hand, acid priming would result in the formation of fresh HyA precipitates, that would likely smother some of negatively charged sites on the soils' original surface (Veerhoff and Brümmer, 1993; Saha *et al.,* 1998), and thus this could account for the decrease in metal cation sorption. This was only observed in the organic and smectitic soils; in the kaolinitic soil there was hardly any change in the adsorption between the untreated and acid-primed soil. The explanation for this could be that there was not much negative charge on the kaolinitic soil's surface to begin with, so the freshly formed HyA precipitates did not alter the surface of the soil with regard to cation sorption. The increase in the metal cation adsorption seen in acid-primed sesquioxidic sample could be attributed to the large amount of Al which is released by this gibbsite-dominated sample. Due to the poorly-ordered structure of the newly formed precipitates, they could have a larger specific area (Harsh and Doner, 1984; Garcia-Sanchez *et al.*, 2002) than the crystalline gibbsite, and thus have a much more reactive surface, thus also resulting in an increase in the metal cation sorption of the soil.

The pH of the solution plays a very important determining role in the specific adsorption of metals on HyA and HAS precipitates on mineral surfaces (McBride, 1994). It has been reported that the formation of these complexes enhances pH-dependent sorption of metals in clays and decrease metal sorption due to cation exchange reactions (Inoue and Satoh, 1993; Lothenbach *et al.*, 1997 &1998; Saha *et al.*, 2001). The pH of the various samples was not recorded during the sorption studies. However, one can make certain assumptions based on pH data from surface charge determinations presented in section 2.3.5. Since the molarity of the $CdCl_2$ solution (12500 mg $Cd.kg^{-1}$ treatment) was about 0.01 M, the likely pH can be approximately inferred as being that measured in 0.01 M KCl. Table 2.5 shows the pH values of the acid-, base-primed and untreated soils in 1:100 suspension in 0.01 M KCl taken from section 2.3.5.

It can be seen that the soil displays a type of "elasticity" in the case of the base-treated soils (Table 2.5), whereby the pH of the soil returns to a higher value after being adjusted to a neutral pH. This is also shown by the pH values measured in water (Table 2.2). Implications of this are that the base-primed soil has a greater negative surface charge due to the higher final pH which thus promotes cation sorption. The untreated and acid-primed have lower final pH values (between 1 and 2 pH units lower – Table 2.5), and thus do not have the same amount of negative surface charge, which can promote cation sorption. This pH-dependent

sorption is further demonstrated by the kaolinitic and sesquioxidic soils, where these two acid-primed soils had a higher final pH than the untreated soils (Table 2.5) and hence showed increased or slightly higher Cd or Cu sorption than the untreated soil (Figs 2.4 & 2.5).

Table 2.5 Soil pH in 1:100 suspension in 0.01 M KCl, in relation to priming treatments.

Soil	Suspension pH in 0.01 M KCl
Organic	
Untreated	4.9
Acid-primed	5.0
Base-primed	6.3
Smectitic	
Untreated	6.9
Acid-primed	6.8
Base-primed	8.4
Sesquioxidic	
Untreated	5.4
Acid-primed	6.5
Base-primed	7.5
Kaolinitic	
Untreated	5.0
Acid primed	5.4
Base primed	7.1

It is likely that solution pH and the type and amount of Al precipitates all play a role in determining the metal cation sorption capacity, with pH possibly having the greatest effect.

The retention of Cd in 12500 $mg.kg^{-1}$ Cd-treated soils after 1 M NH_4NO_3 extraction is shown in Fig. 2.6.

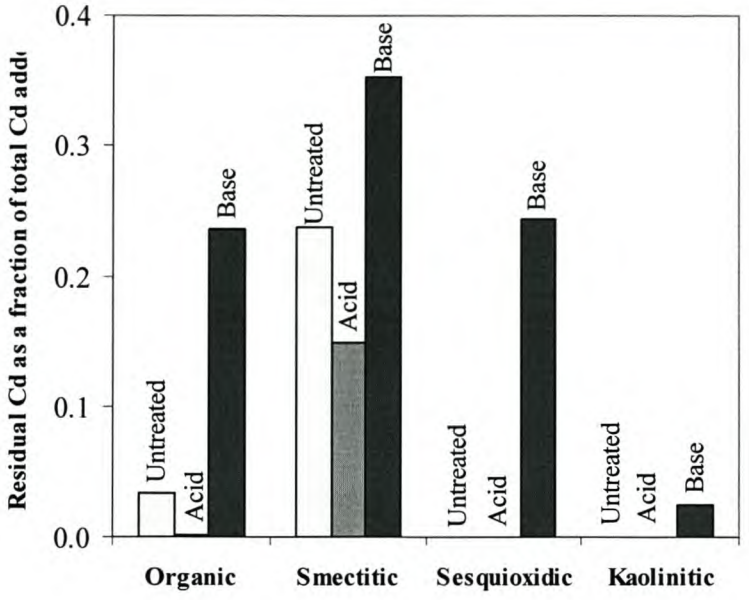


Figure 2.6 Residual sorbed Cd after 1 M NH_4NO_3 extraction of 12500 $mg.kg^{-1}$ Cd-treated soils, as a fraction of total Cd added.

Base-primed soil had the highest proportion of added Cd resistant to NH_4NO_3 extraction. This can especially be seen in the case of the organic and sesquioxidic soil samples (24% and 25% of total Cd added, respectively), when comparing it to the untreated soil. Acid treatment resulted in Cd resistance to NH_4NO_3 extraction than was even lower than in the untreated organic and smectitic soils. This suggests that the new precipitates formed as a result of the acid treatment actually smothered some of the sites where immobilisation of metal cations usually takes place, i.e. they prevent cations from being able to access interlayer and surface positions in the smectitic clay minerals (Sparks, 1995). Effectively no Cd was retained by the sesquioxidic and kaolinitic soils when acid-primed or when untreated (Fig. 2.6).

It is known that Cd is weakly sorbed at pH values below 6 (McBride, 1994), and this is also confirmed by the NH_4NO_3 extraction results (Fig. 2.6) when taking the pH data in Table 2.5 into account. All samples with pH values below 6 show little or no immobilisation of Cd, except for the organic sample that showed some immobilisation despite the low pH. The pH data also confirm why acid priming increased Cd sorption in the sesquioxidic and kaolinitic soils, as the pH of the acid-primed soil was higher than the untreated soil in both cases. Fig. 2.7 shows a comparison of the fraction of Cd: in solution, sorbed and sorbed fraction not extractable by NH_4HO_3 of the acid-, base-primed and untreated soils.

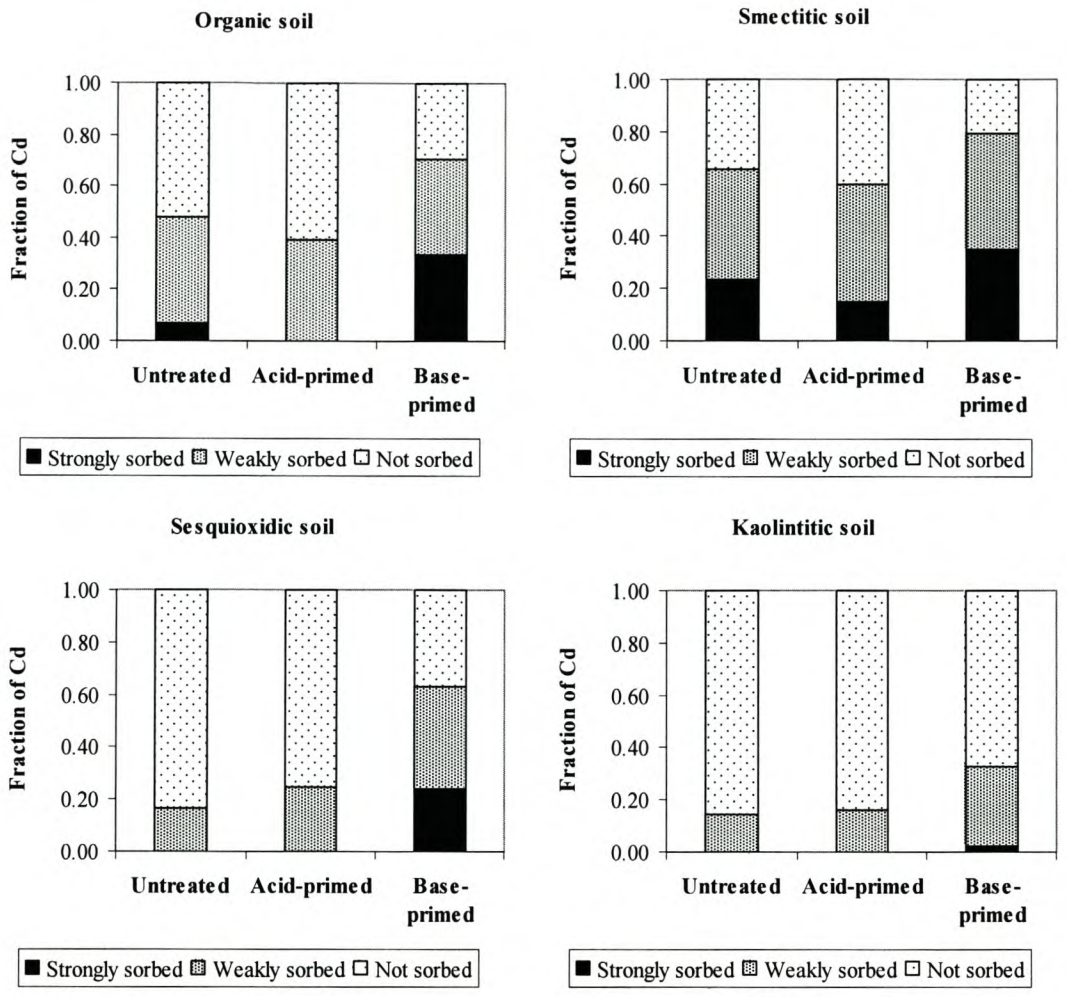


Figure 2.7 Fraction of Cd: not sorbed, weakly sorbed (sorbed fraction extracted by 1 M NH_4NO_3) and strongly sorbed (sorbed fraction not extracted by 1 M NH_4NO_3), of the 12500 $mg.kg^{-1}$ Cd-treated soils.

2.3.3 Phosphate sorption

Phosphate sorption curves for the four soils are shown in Fig. 2.8 & 2.9 in relation to acid and base treatment.

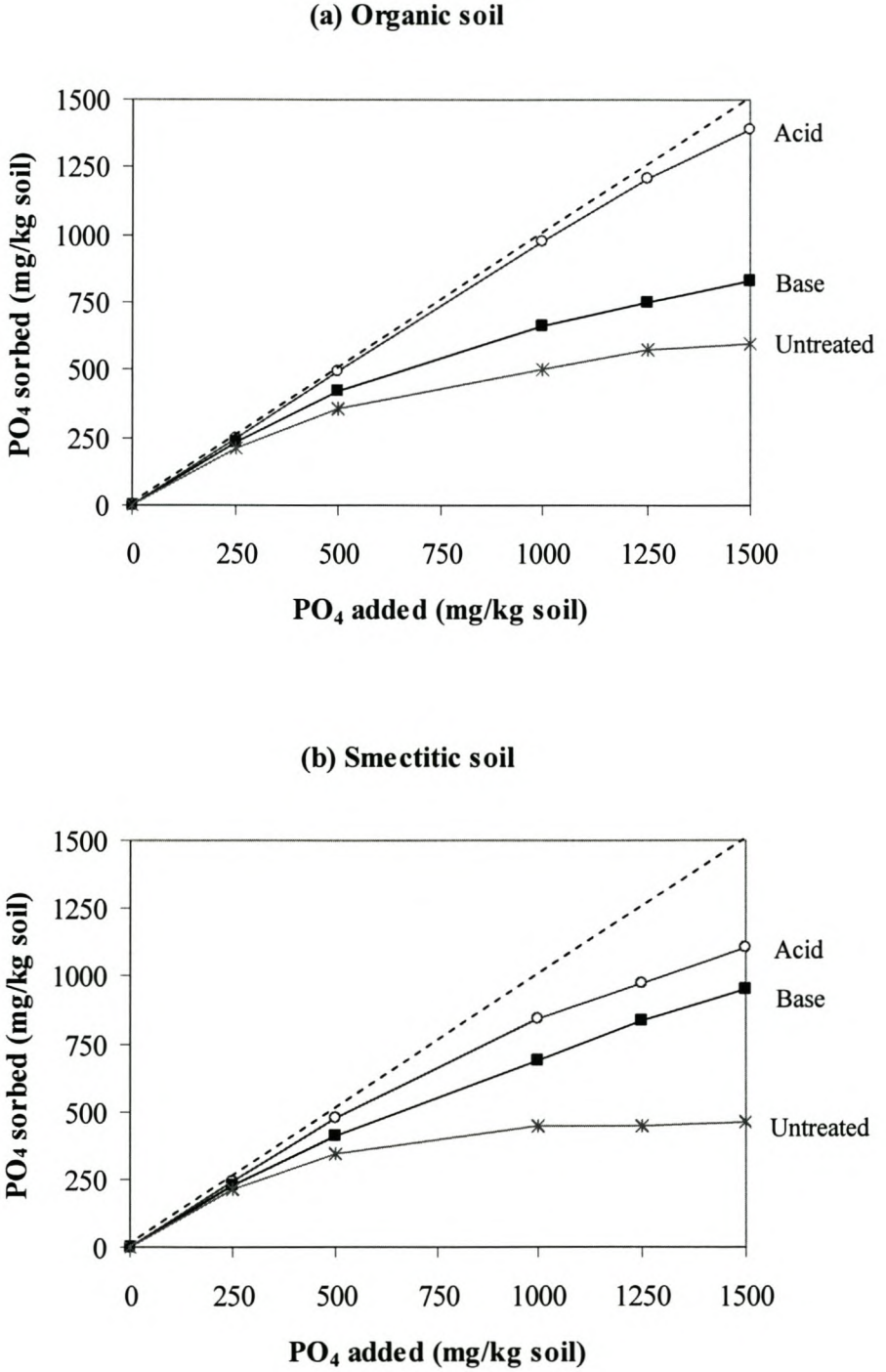


Figure 2.8 Phosphate sorption relative to the amount of phosphate added to acid-, base-primed or untreated soils: (a) organic and (b) sesquioxidic soil (broken line represents complete sorption).

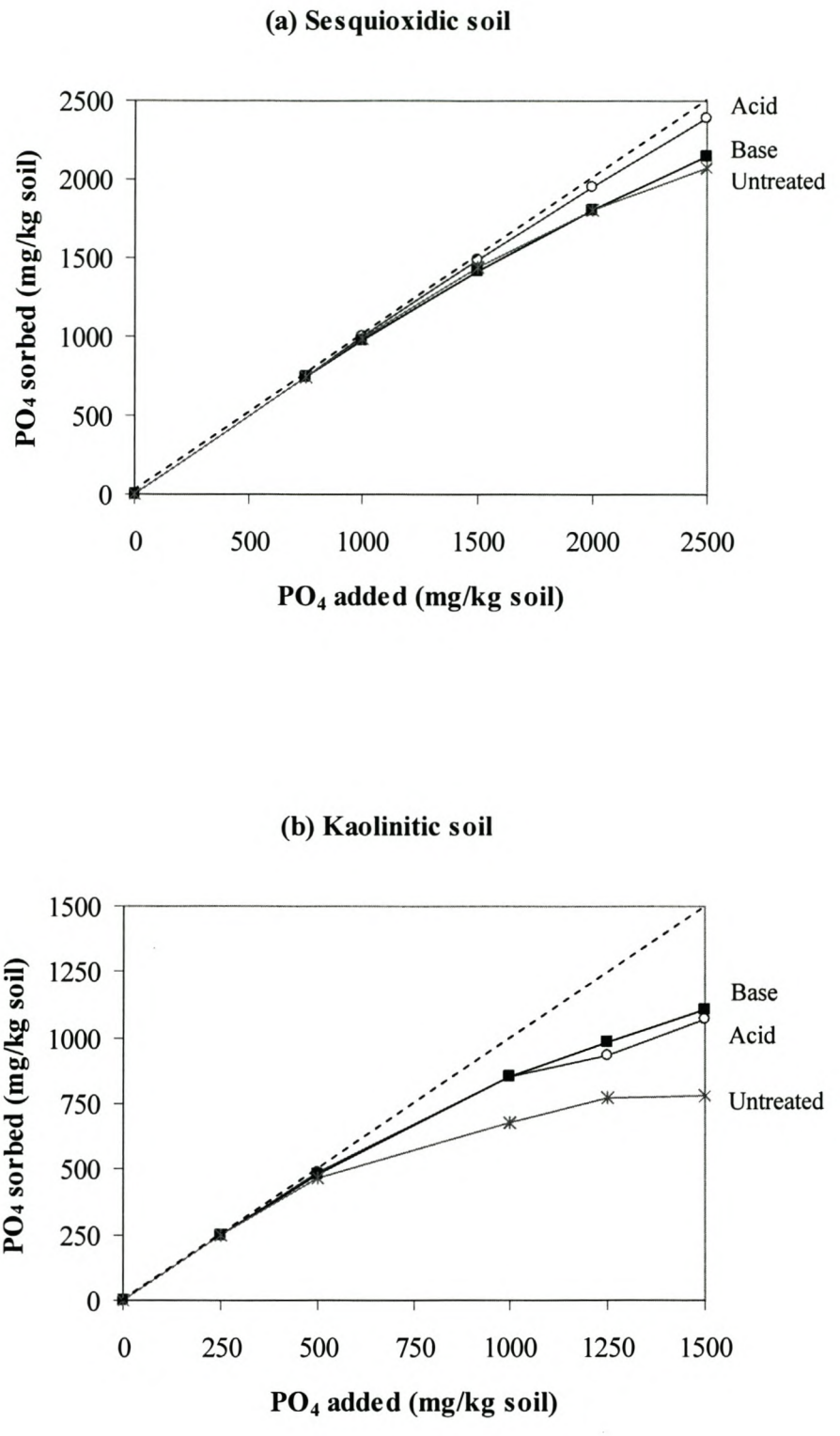


Figure 2.9 Phosphate sorption relative to the amount of phosphate added to acid-, base-primed or untreated soils: (a) sesquioxidic and (b) kaolinitic soil (broken line represents complete sorption).

Acid priming resulted in an increase in the phosphate sorption in all of the soils. This was particularly evident in the case of the organic soil where the increase was almost by 8.4 mmol.kg^{-1} soil which is more than 100% (Fig. 2.8a). Base priming also resulted in an increase in phosphate sorption, but not to the same extent as acid priming. However, in the case of the kaolinitic soil both the acid- and the base-treatments resulted in similar increases in phosphate sorption (Fig. 2.9b). The sesquioxidic soil has such an inherently high phosphate sorbing capacity that only above 1500 mg phosphate.kg^{-1} soil a distinction can be made between sorption curves of the three treatments (Fig 2.9a). Table 2.6 provides a summary of phosphate sorption results for the highest phosphate treatment applied to each soil.

Table 2.6 Summary of phosphate sorption by the four soils in relation to acid- or base-priming treatments.

Soil	PO_4 added (mg.kg^{-1} soil)	PO_4 sorbed (mmol.kg^{-1} soil)	Fraction PO_4 sorbed of total added	Increased sorption following treatment (%)
Organic				
Untreated	1500	6.26	0.40	
Acid-primed	1500	14.7	0.93	138
Base-primed	1500	8.71	0.55	39
Smectitic				
Untreated	1500	4.86	0.31	
Acid-primed	1500	11.7	0.74	141
Base-primed	1500	10.0	0.64	105
Sesquioxidic				
Untreated	2500	21.9	0.83	
Acid-primed	2500	25.2	0.96	15
Base-primed	2500	22.6	0.86	3
Kaolinitic				
Untreated	1500	8.21	0.52	
Acid-primed	1500	11.3	0.72	38
Base-primed	1500	11.6	0.74	41

These observations are confirmed by the study of Saha *et al.* (1998), who investigated the sorption of phosphate on HyA- and HAS-montmorillonite complexes. They also found that HyA and HAS complexes on montmorillonite clay increased phosphate sorption, with the HyA increasing phosphate sorption more than HAS. In the present study, HyA precipitates are most likely to have formed as a result of acid priming, while HAS precipitates are more

likely to have formed during base priming (as discussed in section 2.5.2). This would explain why acid priming generally resulted in a greater increase in phosphate sorption than did base priming.

A possible reason for the kaolinitic soil not showing much difference in phosphate sorption between acid and base treatments is that approximately equal amounts of Al were released during acid and base dissolution of the soil (Table 2.1), so it is likely that the amount of precipitates formed during acid or base priming were the same. However, since the organic soil was also dominated by kaolinite, it is seen that approximately the same amount of Al was also released by the organic soil during acid and base dissolution (Table 2.1). However, there is a remarkable difference in phosphate sorption between the acid- and base-primed organic soil, so it is possible that the high organic matter content accounts for this difference. It is probable that the HyA and HAS precipitates that formed would be more amorphous, due to the presence of organic matter (Lahodny-Šarc and Dragčević, 1981; Violante *et al.*, 1980) and are thus more reactive.

Solution pH also has an important influence on the sorption of phosphate, due to its effect on surface charge. As mentioned in section 2.5.2, HyA and HAS complexes increase the pH-dependent CEC of soils. The higher the pH of the solution the greater is the net negative charge of the soil surface. Since all the base-primed soils had a higher final pH (about 1–2 pH units) than the acid-primed or untreated soils (Table 2.5), it would be expected that this should work against phosphate sorption, but this is not the case. All the base-primed soils show an increase in phosphate sorption, suggesting the formation of new, more adsorptive surfaces. Also, two of the acid-primed samples had higher final pH values than the untreated soils (Table 2.5), namely the organic and kaolinitic soils, yet in both these soils these treatments showed greater phosphate sorption than the untreated soils.

It is likely that solution pH and the type and amount of Al precipitates work together in determining the change in anion sorption. It also seems clear that acid- and base-priming increase the number of functional groups on the surface of the soil which can sorb phosphate.

2.3.4 BET specific surface area

Specific surface area data for two of the soils are shown in Table 2.7.

Table 2.7 BET specific surface area of the sesquioxidic and kaolinitic soils, in relation to acid and base priming.

Soil	Specific surface area ($m^2.g^{-1}$)
Sesquioxidic	
Untreated	60.3
Acid-primed	54.2
Base-primed	52.2
Kaolinitic	
Untreated	31.8
Acid-primed	29.7
Base-primed	28.9

Both the acid and base treatment slightly reduced the external specific surface area (SSA) of the sesquioxidic and kaolinitic soils, the base treatment more so. This is similar to the results of Sakurai and Huang (1998) in the case of base priming, whereby fixation of HAS complexes on a montmorillonite clay, resulted in the decrease of N_2 determined SSA. Similarly to acid priming, Yeoh and Oades (1981a) found that neutralising a montmorillonite and illite clay subjected to acid dissolution with phosphoric acid, resulted in a decrease of the N_2 determined SSA of the clays. They attributed this to the formation of large cluster like precipitates, which formed on the surfaces of the clay minerals, as well on the edges. This suggests that Al-polymeric precipitates cause aggregation sufficient to exclude some surfaces from the N_2 gas molecule used for SSA determination. This implies that enhanced reactivity from priming is due to creation of new surfaces for sorption which are not necessarily more extensive than that which existed originally. In this respect, the term priming has exactly the same connotation as it does in paint technology (surface priming).

2.3.5 Surface charge

Results of surface charge determination are shown in Figs. 2.10 – 2.13. Table 2.8 provides a summary of the corresponding changes in buffer capacity.

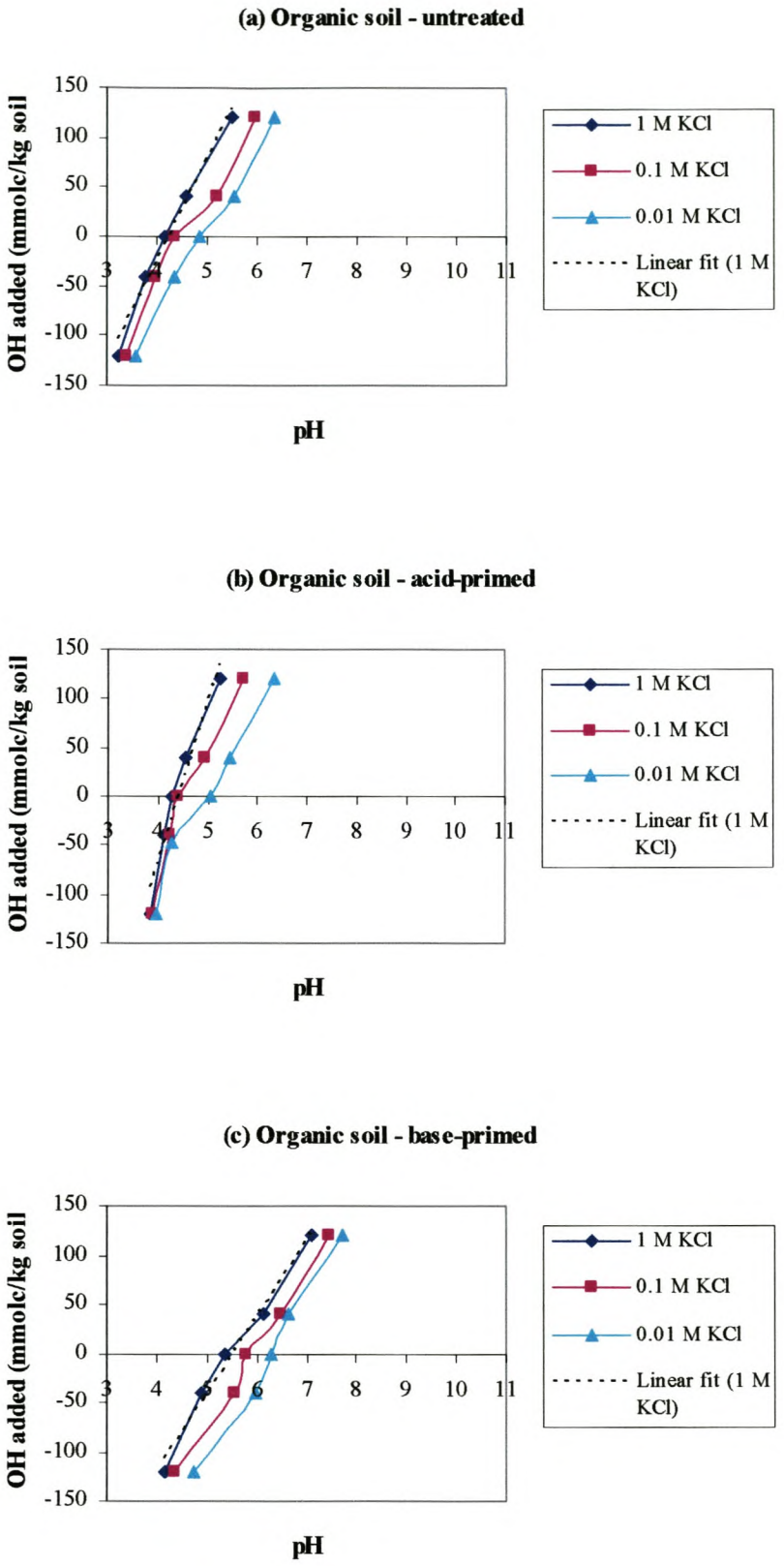


Figure 2.10 Surface charge of the organic soil estimated by equilibration with base or acid (neg. OH axis) as a function of suspension pH at different electrolyte concentrations: (a) untreated, (b) acid-primed and (c) base-primed soils.

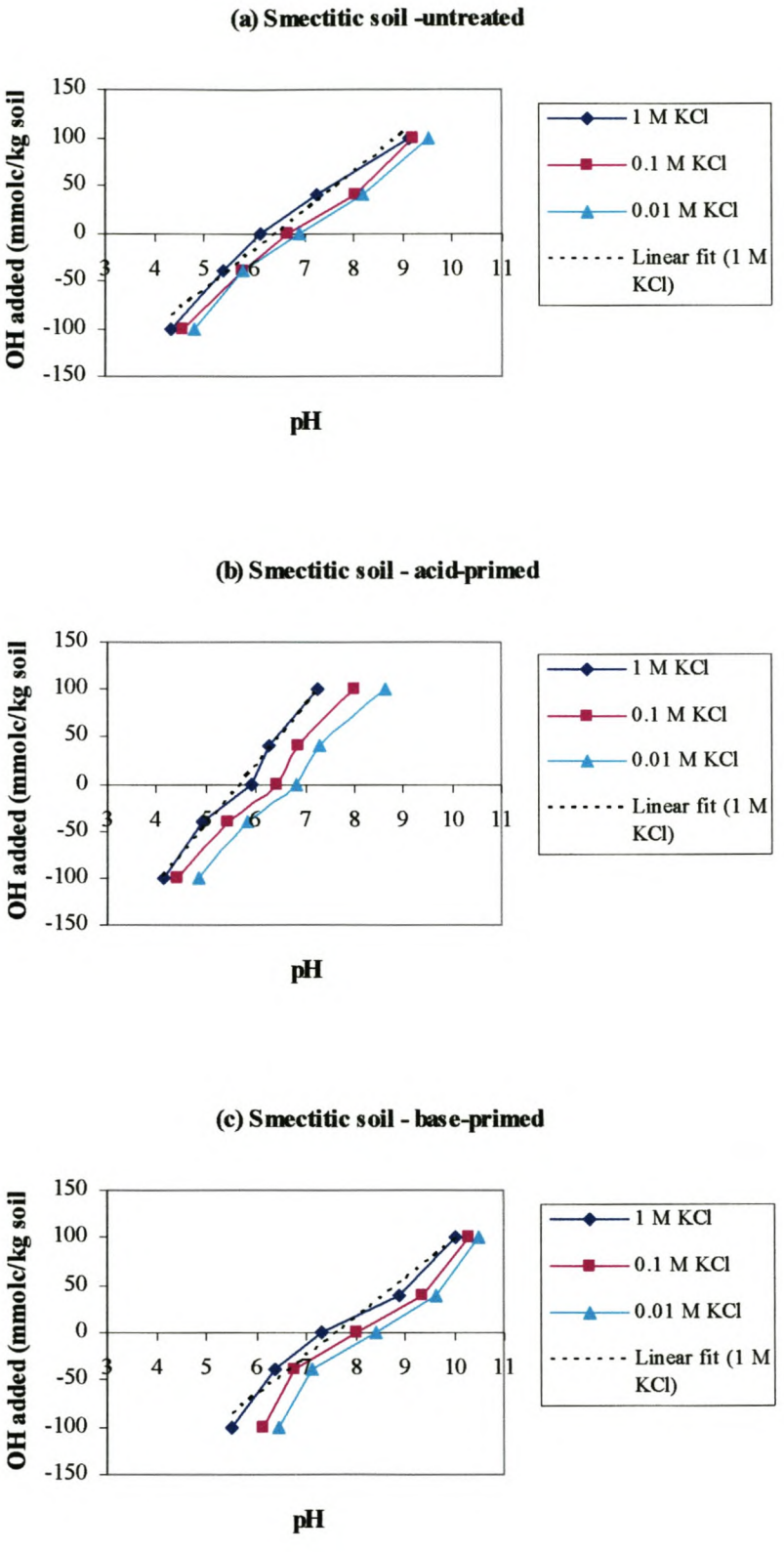


Figure 2.11 Surface charge of the smectitic soil estimated by equilibration with base or acid (neg. OH axis) as a function of suspension pH at different electrolyte concentrations: (a) untreated, (b) acid-primed and (c) base-primed soils.

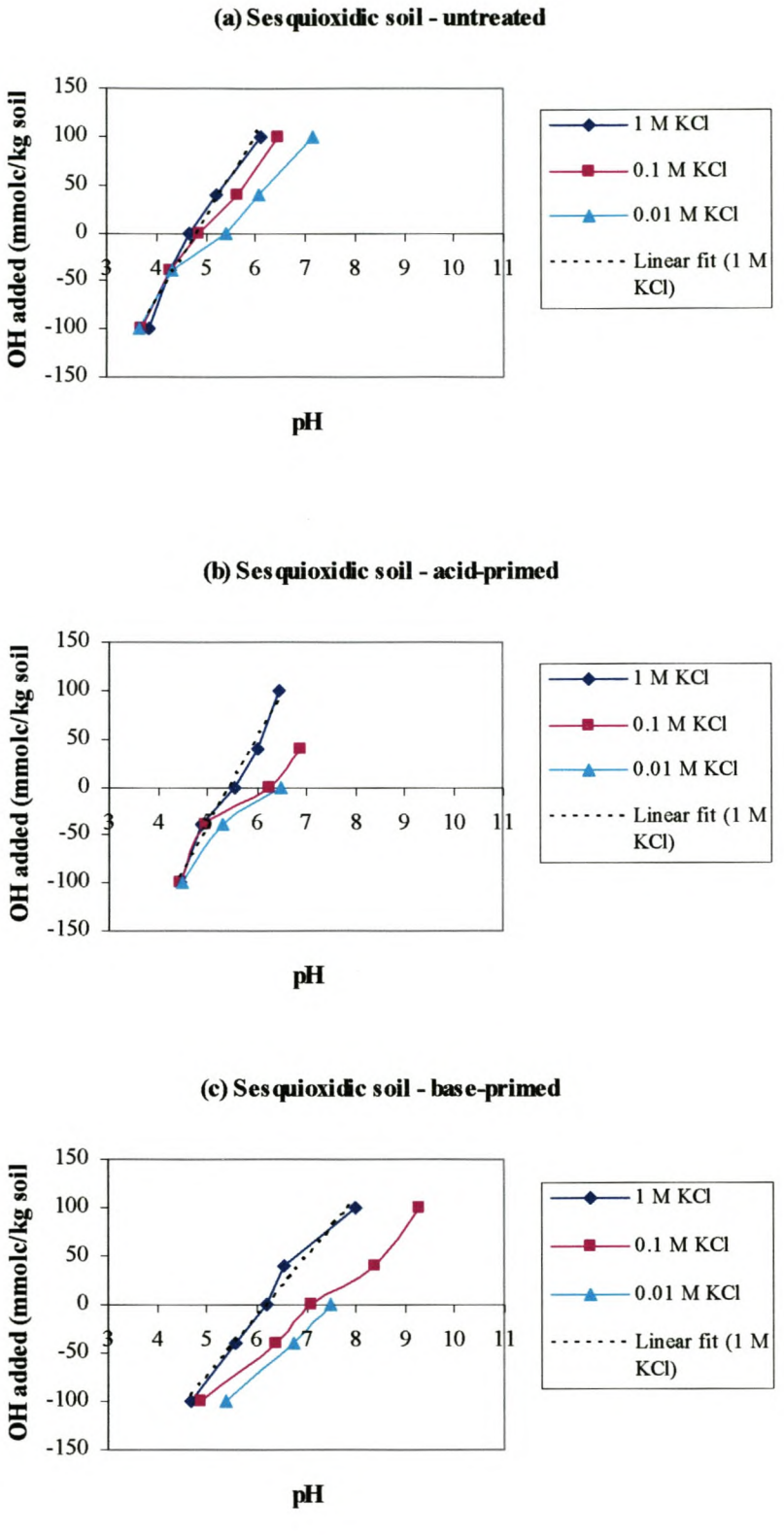


Figure 2.12 Surface charge of the sesquioxidic soil estimated by equilibration with base or acid (neg. OH axis) as a function of suspension pH at different electrolyte concentrations: (a) untreated, (b) acid-primed and (c) base-primed soils.

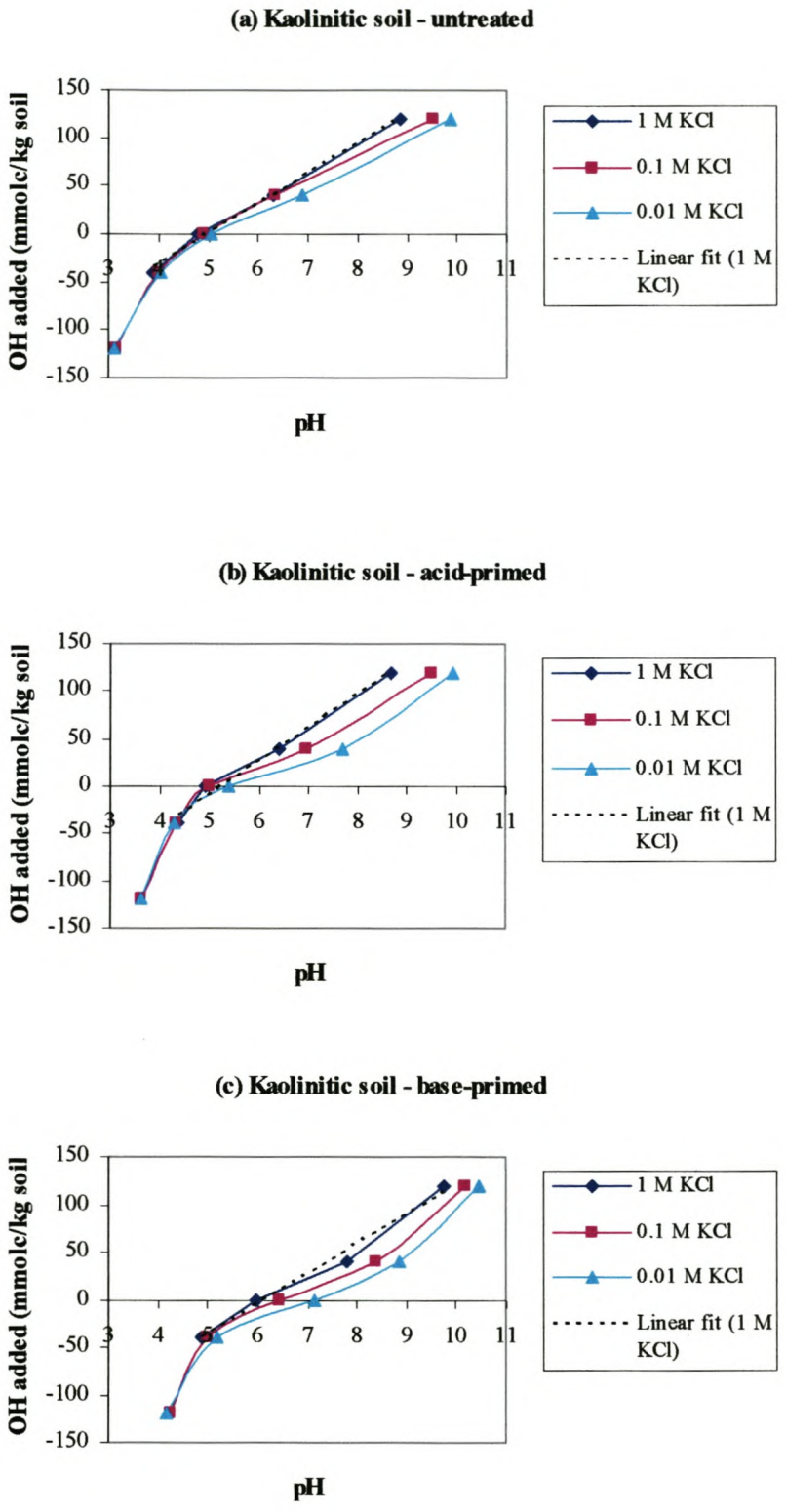


Figure 2.13 Surface charge of the kaolinitic soil estimated by equilibration with base or acid (neg. OH axis) as a function of suspension pH at different electrolyte concentrations: (a) untreated, (b) acid-primed and (c) base-primed soils.

Table 2.8 Estimated gradient of 1 M KCl titration curves in Figs. 2.10 to 2.13.

Soil	Gradient of titration curve (ΔpH/Δmmol OH added)
Organic	
Untreated	104
Acid-primed	163
Base-primed	78
Smectitic	
Untreated	41
Acid-primed	63
Base-primed	41
Sesquioxidic	
Untreated	86
Acid-primed	93
Base-primed	61
Kaolinitic	
Untreated	31
Acid-primed	35
Base-primed	32

Most of the acid- and base-primed soils showed a considerable change in the slope of the titration curve, than compared to the untreated soil (Table 2.8). Acid priming increased the buffer capacity of the soil, whereas base priming decreased it or had little effect. This was particularly evident in the organic and sesquioxidic soils, where the greatest relative increase in the gradient was observed in the acid-primed soils and greatest relative decrease in the base-primed soils. The kaolinitic soil showed the least change in gradient of the titration curves due to acid and base priming.

The observed increase in buffer capacity of the acid-primed soils suggests that acid priming gives rise to more functional groups on the surface of the soil, which can better buffer changes in the soil's pH. It is possible that this could be in the form of more exchangeable Al or variable charge groups. It is possible that the increase in buffer capacity is related to the amount of Al dissolved, and subsequently newly precipitated, during acid priming. If one looks at the Al dissolution data from Chapter 1 (Table 1.2), then it can be seen that the Al release from the soils was in the following order: sesquioxidic > organic > smectitic > kaolinitic. Thus the kaolinitic soil which showed the least dissolution of Al also showed the least change in buffer capacity.

The reason for the base-primed organic and sesquioxidic soils having a reduced buffer capacity is unclear. Possibly it is because there is no longer any exchangeable Al available on the soil surface due to complete neutralisation during base-equilibration, and not retuning the pH to a low enough value during the neutralisation step, to facilitate the formation of exchangeable Al again.

The organic soil (Fig. 2.10), showed no apparent point of zero charge prior to acid priming, but after acid priming there is a tapering of all the buffer curves. This indicates the presence of variable charge material, most probably due to Al oxide formation. Tabulated pH values of the control treatment in 1 M KCl, 0.1 M KCl and 0.01 M KCl are given in Appendix 2, Table A2.5.

2.4 Conclusions

Base priming resulted in an increase in both Cu and Cd sorption capacity of all four soils. Base priming was most effective on the sesquioxidic soil, which also showed the greatest release of Al and Si during equilibration with both strong acid and base. It can be proposed because at a high pH the dissolved Al would be in the tetrahedral coordination, the aluminosilicate precipitate likely to form during neutralisation would probably have some isomorphous substitution of Al for Si (McBride, 1994) and thus would have a permanent negative charge. This could possibly explain the increase in metal cation sorption observed with the base treatment. The higher final pH of the base-primed soils can also partly account for the higher Cd and Cu sorption observed in the all the soils, as a result of pH-dependent CEC.

Acid priming resulted in a decrease in metal cation sorption of the smectitic and organic soils, while there was little effect on the kaolinitic soil. It is likely that the freshly formed Al hydroxy precipitates smother some of the negatively charged sites on the soils' original surface, thus decreasing cation sorption. However, acid pre-treatment resulted in an increase in the cation sorption capacity of the sesquioxidic soil. It can be proposed that this is because the gibbsite is more crystalline than the poorly ordered precipitates that would form and which coat the soil surfaces after priming, and thus create a far more reactive surface. However, there was no indication of any net increase in specific surface area. The

higher final pH of the acid-primed sesquioxidic and kaolinitic soil than the untreated soil, could also account for the increased sorption.

Base priming could be recommended for reducing Cd mobility in the soil, whereas acid priming appeared to be ineffective. This was especially evident by NH_4NO_3 extraction of Cd of the 12500 $mg.kg^{-1}$ Cd-treated soils. Acid priming actually decreased the amount of retained Cd, and in some cases resulted in no Cd being retained at all when NH_4HO_3 extracted.

Acid priming increased phosphate sorption in all four soils. The organic soil showed the greatest response. Base priming was also found to increase phosphate sorption, but not to the same extent as acid priming. This is possibly related to the amount of Al hydroxide precipitate that formed as a result of acid or base priming treatments, and also to the nature of the precipitates formed, as well as the difference in final pH after neutralisation. The phosphate sorption experiment clearly suggested that both acid and base priming of soils results in a new, more reactive surface, which can better sorb phosphate even at higher solution pH values.

Neither acid nor base priming was found to significantly affect the specific surface area of the sesquioxidic or kaolinitic soils. They appeared to slightly decrease it. The surface charge determinations performed on all the treated soils showed that acid priming generally increased the buffer capacity of the soil, while base priming decreased it, or had little effect.

Acid priming could be used to improve the anion sorption capacity of a soil. Phosphate is known to show the same adsorption behaviour as arsenate (O'Neill, 1995), and thus acid priming could be used to increase the adsorption capacity of a soil with regards to more harmful anions. A practical application of this would be for decontaminating water by passing it through the treated soil. Soils high in oxides have been demonstrated to effectively remove contaminants such as arsenate (Garcia-Sanchez *et al.,* 2002) or fluoride (Wang and Reardon, 2001; Chidambaram *et al.*, 2003; Coetzee *et al.,* 2003), which are problem contaminants in drinking water in particular in India, and even some parts of South Africa. The use of soil has received special attention as of late, specifically because it could be cheap and simple method of decontaminating water, compared to other more expensive and advanced treatments that are available in the first world.

Sorption studies which take pH-dependent sorption into account would have been more revealing and would have given a clearer indication of the actual increases in sorption due to priming. This is because HyA and HAS complexes on mineral surfaces have been found to increase the pH-dependent sorption of metals ((Inoue and Satoh, 1993; Lothenbach *et al.*, 1997 &1998; Saha *et al.*, 2001). However, it is important to realise that in a field situation it would be difficult to control the pH of the soil uniformly and thus, as an initial approximation these experiments suffice to show that the sorption capacity of the soil can be enhanced using simple acidification or alkalisation and then neutralising it.

3 ACID/BASE TREATMENT FOR DECONTAMINATION

3.1 Introduction

Taylor (1984) suggested that pH-controlled precipitation reactions could play an important role in soil pollution control because they could more effectively remove heavy metal cations from solution than could adsorption processes involving the same species. The objective of this chapter is to explore the possibility of coprecipitating divalent metal contaminants with released Al, Si and Fe from acid or base dissolution, during the neutralisation step of the acid- or base-priming technique.

In the first of two experiments to achieve this objective, two metals with contrasting characteristics were chosen, namely Cd(II) and Cu(II). Cadmium has a larger ionic radius than Cu, and is weakly sorbed on organic matter, silicate clays and oxides unless the pH is higher than 6. Copper is a strongly complexing metal, and is strongly adsorbed on the colloidal material of soils (McBride, 1994). In the second experiment, the effectiveness of the acid-base pairs HCl-KOH and H_2SO_4-$Ca(OH)_2$ was compared with regard to removing Cu(II) from solution. Due to the large amount of salt which is generated during the neutralisation of the acid or base additions, it is important to take into account the effect this salt would have on a soil. High concentrations of salt make soils inhospitable for plants, and if a relatively benign salt such as gypsum were generated, this might actually improve soil structure. The effect of ionic strength on metal solubility was therefore also investigated in the second experiment.

The following literature review takes a brief look at the chemical principles involved in the precipitation of the reaction products of dissolution reactions, with emphasis being given to the formation of mixed cation hydroxide phases on mineral surfaces.

Aluminium and Si co-precipitate in the pH range of 4 to 11 (McBride, 1994). There has been much work done on the coprecipitation of double metal hydroxides by raising the pH of solutions containing a trivalent and a divalent metal cation, especially involving hydroxy Al compounds (Brown and Gustache, 1967; Gastuche *et al.*, 1967; Taylor, 1984; Thevenot

et al., 1989; Hansen *et al.*, 1990; Scheidegger *et al.* 1997). The ionic radius of metals dictates whether a metal will form such a double-metal hydroxide compound or not. Smaller cations such as Cu(II), Ni(II) and Zn(II) readily form such compounds.

Taylor (1984) examined the "induced hydrolysis" process whereby a trivalent metal cation hydrolyses at a lower pH than that of the divalent cation and induces the divalent cation to precipitate as a double metal hydroxy compound. Taylor stated that this type of process should be found in natural environments during mineral weathering if two elements are separated by differences in pH-dependent solubility.

Scheidegger *et al.* (1997) studied the formation of mixed-cation hydroxide phases of Ni and Al on the surfaces of clays and Al oxides. They found spectroscopic evidence for the formation of these precipitates on the surfaces of kaolinite, montmorillonite, pyrophyllite and gibbsite. They demonstrated that Ni/Al hydroxide-like compounds can form when Ni is introduced into an environment with a source of hydrolyzed species of Al.

Ford *et al.* (2001) reviewed all surface complexation models currently implemented, including two models for coprecipitation. The one model involved the contribution of components from the mineral surface, specifically applying to environments where surfaces are undergoing weathering. The other model involved the mineral surface directing coprecipitation by lowering the energy barrier to precipitation, i.e. by providing a structural template. They also highlighted the current shortcomings in spectroscopic techniques which are used to identify and characterise precipitates in complex material such as soil.

3.2 Materials and methods

3.2.1 Effect of acid and base treatment on Cd and Cu solubility

The smectitic and kaolinitic soils investigated in Chapters 1 and 2 were used in this experiment (Table 1.1). Each acid or base treatment involved three stages. In the first stage Cd or Cu solution was added to soil and equilibrated for 24 h. In the second stage an aliquot of acid or base was added to the Cd- or Cu-equilibrated suspension and then equilibrated for 5 days. In the third stage the acid- or base-equilibrated suspension was neutralised to pH 6.5 by means of slow titration. Samples were sampled at the end of each stage mentioned, by

centrifuging and filtering to separate the soil from the solution and the amount of Cd, Cu, Al, Si and Fe was determined in the supernatant. The solution pH was also measured after each stage. In the original design of the experiment there were three replicate samples for each soil treatment's sampling stage, i.e. three for the 24 h sorption period, three for the acid equilibration, three for the base equilibration and three for the neutralisation of the acid-equilibration and three for the neutralisation of the base equilibration. However, there was only one sample for each acid or base treatment neutralisation stage.

The first stage of acid or base treatment involved adding 50 ml 500 $mg.L^{-1}$ Cd^{2+} ($CdCl_2.H_2O$) or Cu^{2+} ($CuCl_2.2H_2O$) to 5g soil and this was shaken for 24 hours in sealed polyethylene bottles. At the end of this period samples were taken as described above. To the remaining samples, 5 ml 1 M HCl or KOH was added and then returned to the shaker for a period of 5 days of vigorous shaking. The concentration of the HCl or KOH in each suspension was approximately 0.09 M and the pH values of the solutions were 1.2-1.3 and 12.8-12.9, respectively. After this shaking samples were again taken, as described above. The remaining samples were then titrated (Mettler DL21) using 1 M HCl or KOH to pH 6.5 over a period of approximately 6 h. Titration curves are shown in Appendix 3, Fig. A3.3. The supernatants of the neutralised samples were then collected as described above. The concentration of Cd, Cu, Al, Si and Fe was determined in the supernatants using an ICP-OES (Varian Vista Pro) equipped with a CCD spray chamber, a Meinhard type nebulizer and external calibration. Cadmium and Cu concentrations were also determined using an ICP-MS (Perkin-Elmer Sciex Elan 6000) equipped with a quadrupole mass filter, a Scott type spray chamber and a Meinhard type nebulizer. External calibration was used on the ICP-MS but rhodium was added to the samples and standards as an internal standard for drift correction. The reproducibility of the ICP determinations are shown in Appendix 3, Tables A3.1 – A3.3.

3.2.2 The effect of acid-base pair and ionic strength on Cu solubility

3.2.2.1 Soil characterisation

Two South African soils were used for this final experiment, both provided by M.V. Fey who originally sampled them in Kwazulu-Natal in 1973. The one is a dark topsoil of a Vertisol (Arcadia form – Soil Classification Working Group, 1991) derived from dolerite (Creighton district) and the other one is a red subsoil of an oxisol (Griffin form – Soil

Classification Working Group, 1991) derived from mixed dolerite-shale colluvium (Donnybrook district). Salient properties are given in Table 3.1.

Table 3.1 Summary of the characteristics of the South African soils.

Soil sample	pH H_2O	pH KCl	% C	% Clay	Dominant clay minerals
Arcadia	6.5	5.1	3.2	46	2:1 layer silicates
Griffin	5.2	4.3	0.6	55	Kaolinite & some gibbsite

Soil pH was determined in a 1:2.5 soil suspension in distilled water or 1 M KCl. The clay content was determined by the pipette method after dispersion in calgon (Gee and Bauder, 1986). Total carbon was determined using a Eurovector elemental analyzer.

XRD was performed on the clay fraction, smeared on glass slides using a Philips 1404 diffractometer equipped with CuKα radiation (40 mA, 50 kV) and a graphite monochromator, by step scanning at a rate of $1°2\theta.min^{-1}$ ($0.05°2\ \theta$ step size). The x-ray diffractograms are included in Appendix 3, Figs. A3.1 – A3.3. The clays were separated from the rest of the soil fractions using the method described in Appendix 3.

3.2.2.2 Acid and base treatment

Similarly to the first experiment (section 3.2.1), each acid or base treatment involved three stages. In the first stage Cu solution was added to soil and equilibrated for 24 h. In the second stage an aliquot of acid or base was added to the Cu-equilibrated suspension and then equilibrated for 7 days. In the third stage the acid- or base-equilibrated suspension was neutralised to pH 5-7 by adding a sufficient amount of acid or base and shaking overnight. Samples were sampled at the end of each stage mentioned, by centrifuging and filtering to separate the soil from the solution and the amount of Cu was determined in the supernatant. The pH and EC of the solution was also measured after each stage. In this experiment there were two replicate samples for each soil treatment's sampling stage, i.e. two for the 24 h sorption period, two for the acid equilibration, two for the base equilibration and two for the neutralisation of the acid-equilibration and two for the neutralisation of the base equilibration.

There were three different acid and base treatments for each soil. Similar to the first experiment (section 3.2.1), in the first treatment HCl and KOH were used with no background electrolyte. In the second treatment HCl and KOH were used as acid-base pair

with a 0.1 M KCl background electrolyte, and in the third treatment H_2SO_4 and $Ca(OH)_2$ were used as acid-base pair with a 0.1 M KCl background electrolyte.

The first stage of acid or base treatment involved adding 25 ml 500 $mg.L^{-1}$ Cu^{2+} ($CuCl_2.2H_2O$) dissolved in 0.1 M KCl or distilled water, to 2.5g soil, and this was shaken for 24 hours in sealed polyethylene bottles. At the end of this period samples were taken as described above. To the remaining samples an aliquot of acid or base was added (Table 3.2) and then returned to the shaker for a period of 7 days of vigorous shaking. The concentration of the acid or base in each solution was approximately 0.09 M and the pH values of the solutions were 1.1-1.2 and 12.8-12.9 (12.4 in $Ca(OH)_2$ treated samples), respectively. After this shaking samples were taken, as described above. The remaining two samples of each treatment were then neutralised using the appropriate amount of acid or base to approximately pH 6.5 (Table 3.2) and shaken overnight. The amount of acid or base required for adjusting the pH was determined by slowly titrating a trial acid- or base-equilibrated sample with HCl or KOH until pH 6.5 was reached. Then the same molar quantity of acid or base was then added to the actual samples to achieve a similar pH and shaken overnight (Table 3.5). The solutions of the neutralised samples were then collected as described above. The concentration of Cu in the supernatants was determined using flame AAS (Varian Spectr AA 250 Plus).

Table 3.2 Amount and type of acid or base added to the soils during the acid and base treatments of Cu-treated Arcadia and Griffin soils.

	Acid/base added for equilibration	**Acid/base added for neutralisation**
Acid treatments		
Arcadia (HCl-KOH, water)	1.25 ml 2 M HCl	1.45 ml 2 M KOH
Arcadia (HCl-KOH, 0.1 M KCl)	1.25 ml 2 M HCl	1.45 ml 2 M KOH
Arcadia (H_2SO_4-$Ca(OH)_2$, 0.1 M KCl)	1.25 ml 1 M H_2SO_4	0.124 g $Ca(OH)_2$
Griffin (HCl-KOH, water)	1.25 ml 2 M HCl	1.60 ml 2 M KOH
Griffin (HCl-KOH, 0.1 M KCl)	1.25 ml 2 M HCl	1.60 ml 2 M KOH
Griffin (H_2SO_4-$Ca(OH)_2$, 0.1 M KCl)	1.25 ml 1 M H_2SO_4	0.123 g $Ca(OH)_2$
Base treatments		
Arcadia (KOH-HCl, water)	1.25 ml 2 M KOH	0.85 ml 2 M HCl
Arcadia (KOH-HCl, 0.1 M KCl)	1.25 ml 2 M KOH	0.85 ml 2 M HCl
Arcadia ($Ca(OH)_2$-H_2SO_4, 0.1 M KCl)	0.093 g $Ca(OH)_2$	0.85 ml 1 M H_2SO_4
Griffin (KOH-HCl, water)	1.25 ml 2 M KOH	0.95 ml 2 M HCl
Griffin (KOH-HCl, 0.1 M KCl)	1.25 ml 2 M KOH	0.95 ml 2 M HCl
Griffin ($Ca(OH)_2$-H_2SO_4, 0.1 M KCl)	0.093 g $Ca(OH)_2$	0.90 ml 1 M H_2SO_4

The reproducibility of the AAS Cu determinations is shown in Appendix 3, Table A3.4.

3.3 Results and discussion

3.3.1 Effect of acid and base treatment on Cd and Cu solubility

The solubility of Cd and Cu added to the two soils after (i) 24 h equilibration, (ii) 5 days of acid or base equilibration and (iii) neutralisation to pH 6.5 is shown as a fraction of the initial metal concentration in solution in Fig. 3.1 & 3.2. Corresponding pH measured in the supernatant solution are shown in Table 3.3.

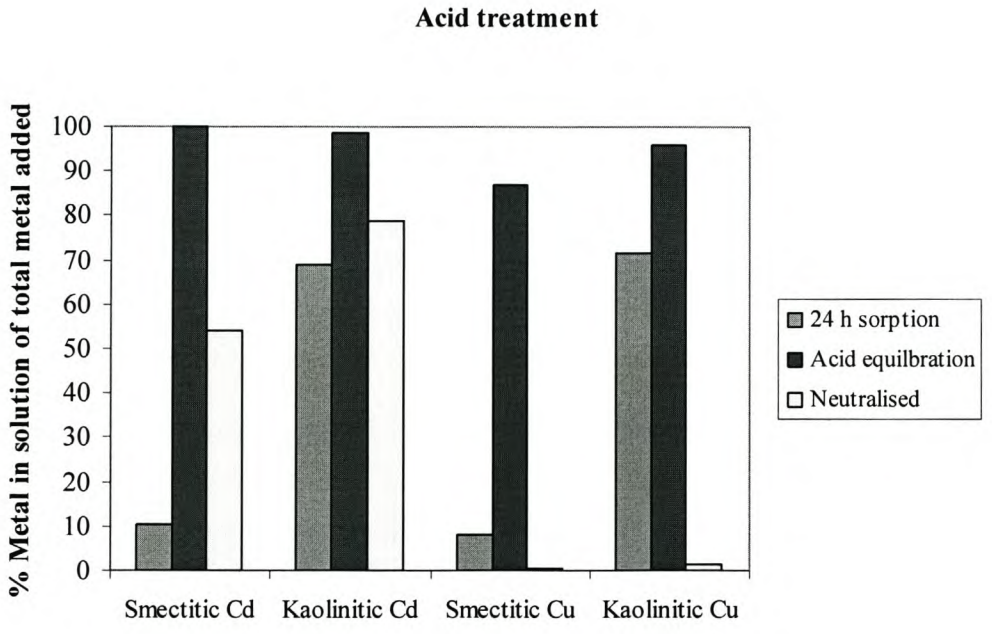


Figure 3.1 Results of the acid treatment on smectitic and kaolinitic soils, comparing percentage Cd and Cu of total added in solution at the three stages in the treatment.

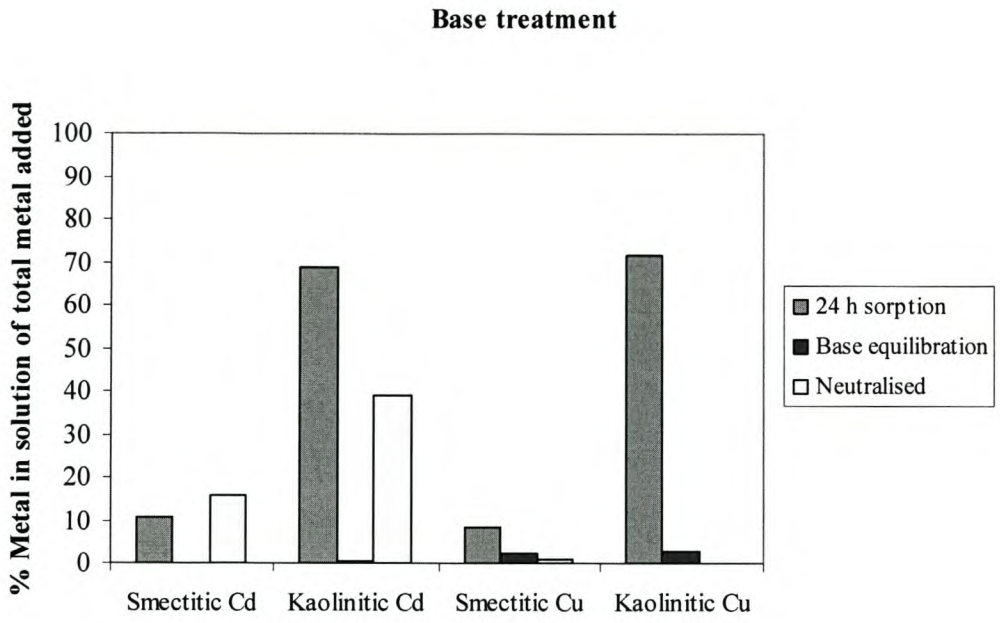


Figure 3.2 Results of the base treatment on smectitic and kaolinitic soils, comparing percentage Cd and Cu of total added in solution at the three stages in the treatment.

Table 3.3 The mean suspension pH of the Cd- and Cu-treated smectitic and kaolinitic soils at the various stages in the acid- and base-treatments

	Sorption	**Acid/base equilibration**		**Neutralisation**
	After 24 h shaking with metal	Before 5 days shaking	After 5 days shaking	Before filtration
Acid treatments				
Smectitic Cd	6.5	1.2	1.6	5.8
Smectitic Cu	5.0	1.2	1.5	5.9
Kaolinitic Cd	4.8	1.2	1.3	5.6
Kaolinitic Cu	4.1	1.2	1.2	6.1
Base treatments				
Smectitic Cd	6.5	12.9	12.7	6.8
Smectitic Cu	5.0	12.8	12.8	-
Kaolinitic Cd	4.8	12.9	12.8	6.6
Kaolinitic Cu	4.1	12.9	12.8	6.5

The acid and base treatments were most effective at removing Cu from solution, whereas, Cd actually increased in availability after the treatments (Fig 3.1 & 3.2). The only exception was the Cd-treated kaolinitic soil that was base-treated (Fig. 3.2), where 30% less Cd was in solution than before treatment. It is possible that this decrease is related to the amount of Al

released during the base equilibration. The Al released during basic dissolution by the kaolinitic soil was much higher (12.3 $mmol.kg^{-1}$ soil) than the smectitic soil (2.3 $mmol.kg^{-1}$ soil), thus more Al precipitate was formed which could sorb Cd. Acid and base treatments were the most effective in reducing Cu availability in the kaolinitic soil, where the amount of available Cu was decreased from approximately 72% to 1.5% and 0.2%, respectively.

It is probable that the newly formed, positively-charged Al hydroxy precipitates actually smother some of the sites of negative charge which were originally present on the surface of the soil. This could explain the increase in Cd in solution after the treatment than compared to before, specifically because Cd is sorbed by simple cation exchange mechanisms (McBride, 1994). This is particularly evident in the smectitic sample, where the increase in Cd in solution was almost by 40%. Furthermore, there is a large amount of salt (KCl) generated during the neutralisation of the acid or base, and it is possible that K^+ ions are competing with Cd for exchange sites.

Base equilibration resulted in all Cd being removed from solution, and this is expected as Cd precipitates as $CdCO_3$ and other hydroxy compounds above pH 7 (McBride, 1994; Lindsay, 1979). During acid equilibration practically all Cd added was available, and this is likely as Cd is highly soluble under acidic conditions (McBride, 1994).

However, base equilibration did not remove all the Cu from solution and this is probably because at high concentrations of Cu and at a high pH, Cu forms soluble hydroxy, carbonate and organic matter complexes (McBride, 1994; Lindsay, 1979). The Cu^{2+} ion is predominant in solution at a pH below 6.9 (Lindsay, 1979) and thus almost all of the Cu was in solution during the acid equilibration period. However Cu^{2+} has a high affinity for the colloidal material of soils (McBride, 1994) and thus some Cu remains unavailable even at the extremely low pH (Fig. 3.1). This affinity increases with increasing pH and thus explains the effective removal of most of the Cu from solution by neutralisation of the soil solution to pH 6.5. If a soil contains a high Cu concentration, then the Cu can precipitate as cupric hydroxide, oxide or hydroxy-carbonates above pH 6 (Mc Bride 1994). Due to its small size Cu^{2+} is able to form solid solutions with Al hydroxide known as the hydrotalcites, with the general formula $\left[M^{2+}_{1-x}Al_x(OH)_2\right]^{x+} A^{n-}_{x/n}$ where A^{n-} is an anion such as Cl^- or CO_3^- (Taylor, 1984; Thevenot *et al.*, 1989; McBride, 1994). Cd is unable to form such precipitates with Al

hydroxide because of its larger ionic radius. It could be possible that these types of double metal co-precipitates form with Cu during the neutralisation reaction of the acid treatment.

The amount of the contaminating metal cation, Al, Fe and Si in solution expressed per unit mass of soil, at the various sampling stages during the contaminant availability study for each of the following treatments: Cd- and Cu-treated smectitic and kaolinitic soils, are shown in Figs. 3.3 – 3.6, respectively.

It is interesting to observe that the acid treatments on the Cd-treated smectitic and kaolinitic soil (Fig. 3.3a & 3.5a) resulted in a much greater dissolution of Al than those treated with Cu (Fig. 3.4a & 3.6a). This trend is also slightly noticeable in the base treatment. It appears that the presence of Cu decreases Al dissolution during the acid equilibration. This could mean that Cu forms a Cu hydroxy or Cu-Al hydroxy (Taylor, 1984; Thevenot *et al.*, 1989) precipitate on the surface of the mineral, as a result of mass action due to the high Cu concentration in solution (5000 $mg.l^{-1}$). This Cu-hydroxy precipitate then creates a zone of higher pH which could act as a barrier and shields the mineral surface from proton attack. It is known that Cu has a high affinity for soil colloids even at extremely low pH values (McBride, 1994).

Acid equilibration showed a much greater dissolution of Al and Si, than did base equilibration. This concurs with dissolution results presented in Chapter 1.

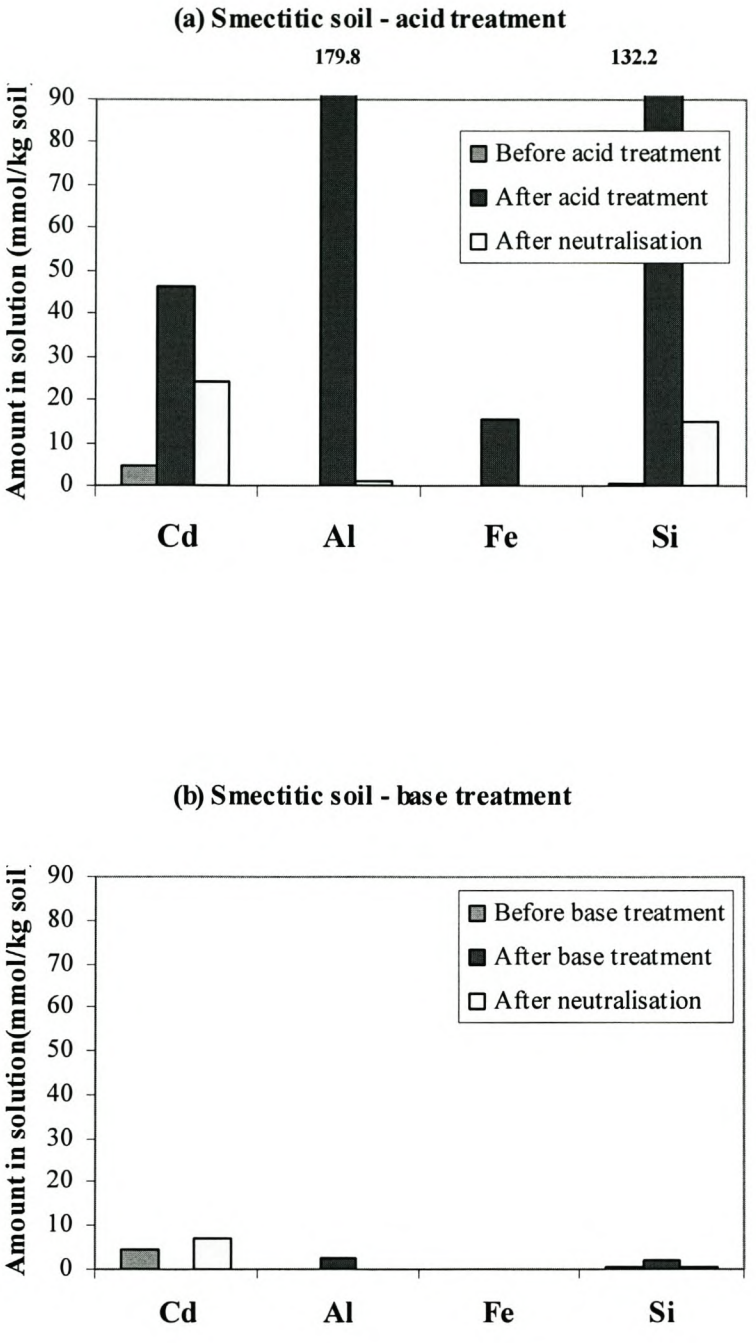


Figure 3.3 Amount of Cd, Al, Fe and Si in solution (expressed per unit mass of soil) at the three stages in the (a) acid- and (b) base-treatment of the Cd-treated smectitic soil.

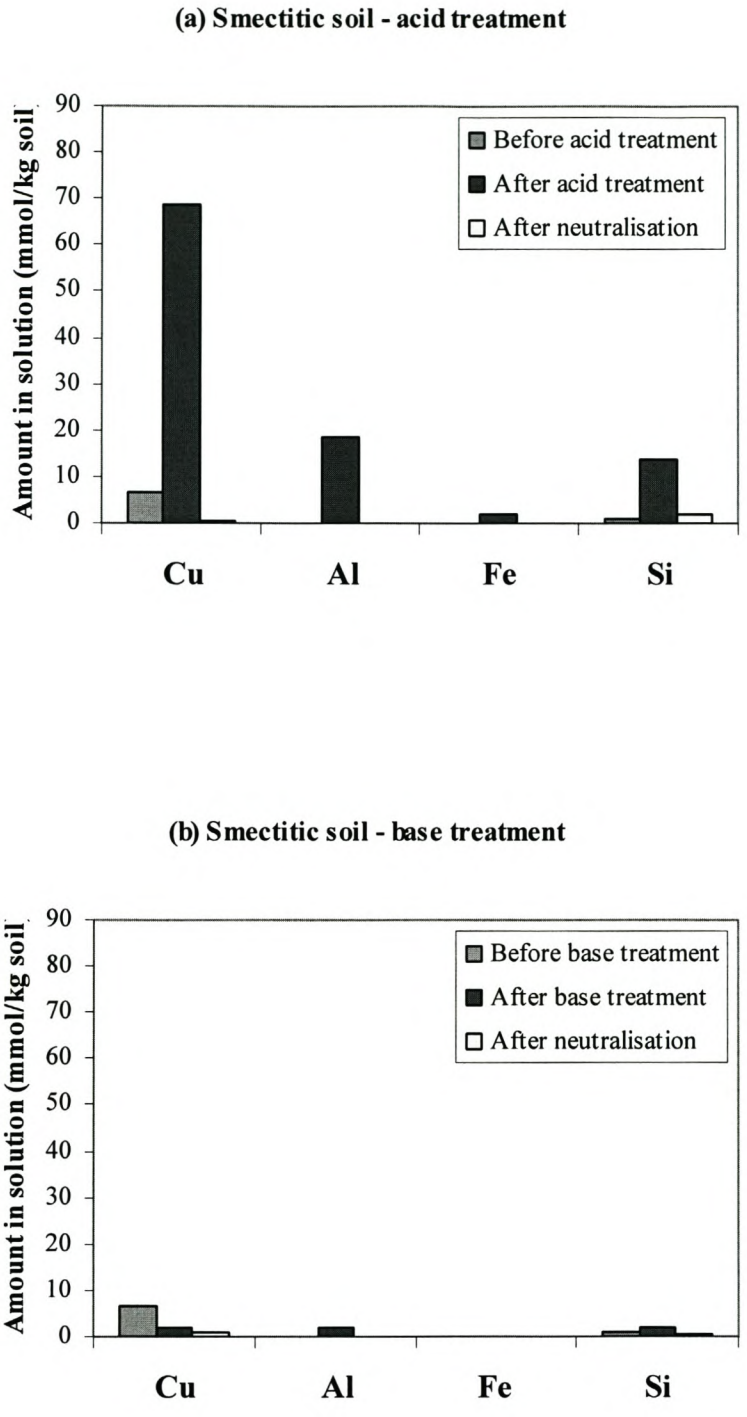


Figure 3.4 Amount of Cu, Al, Fe and Si in solution (expressed per unit mass of soil) at the three stages in the (a) acid- and (b) base-treatment of the Cu-treated smectitic soil.

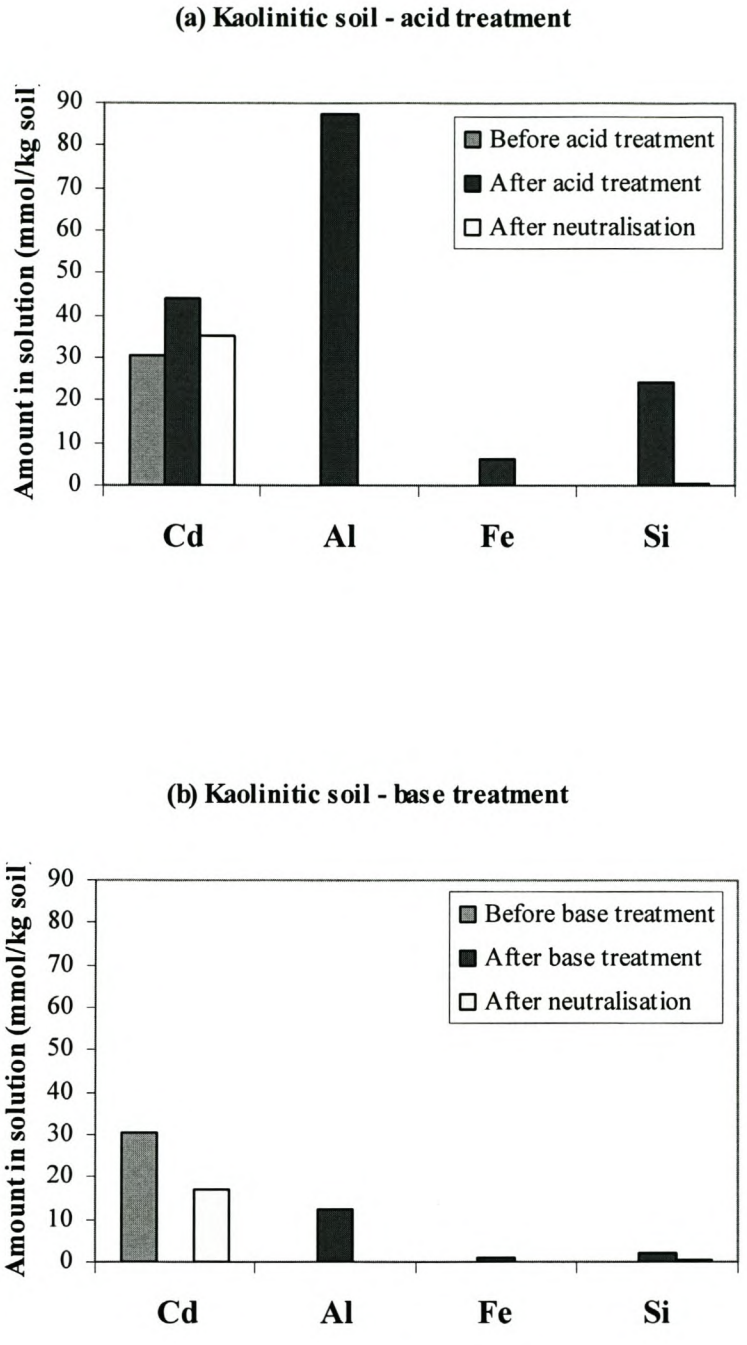


Figure 3.5 Amount of Cd, Al, Fe and Si in solution (expressed per unit mass of soil) at the three stages in the (a) acid- and (b) base-treatment of the Cd-treated kaolinitic soil.

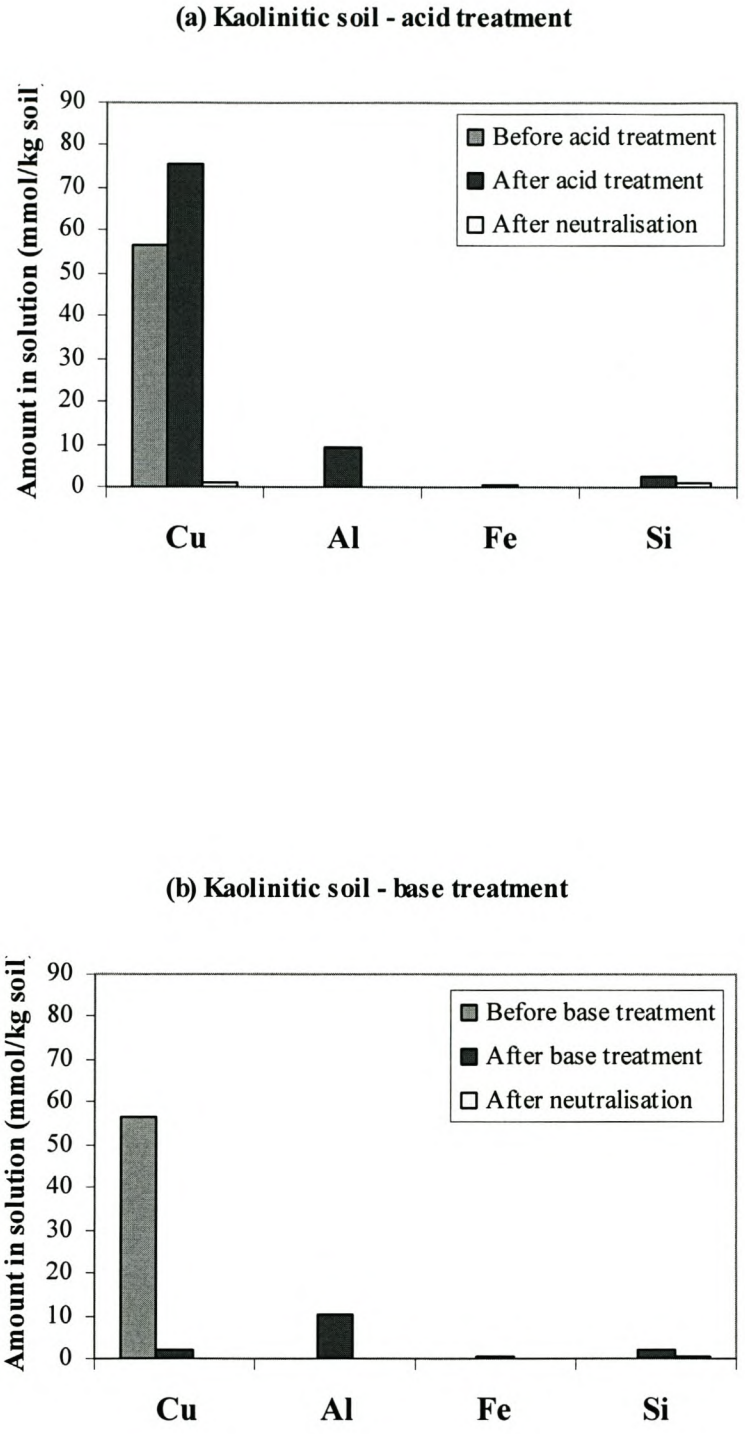


Figure 3.6 Amount of Cu, Al, Fe and Si in solution (expressed per unit mass of soil) at the three stages in the (a) acid- and (b) base- treatment of the Cu-treated kaolinitic soil.

3.3.2 The effect of acid-base pair and ionic strength on Cu solubility

Figs. 3.7 - 3.10 show the solubility of Cu (as a fraction of the initial Cu concentration in solution) at the various sampling stages in acid and base treatments of the Arcadia and Griffin soils, using different acid- and base-pairs, namely HCl-KOH and H_2SO_4-$Ca(OH)_2$, and also comparing the effect of the presence or absence of a background electrolyte, namely 0.1 M KCl. Table 3.4 provides a summary of the Cu concentrations (mmol.kg^{-1} soil) in solution during the acid and base treatments.

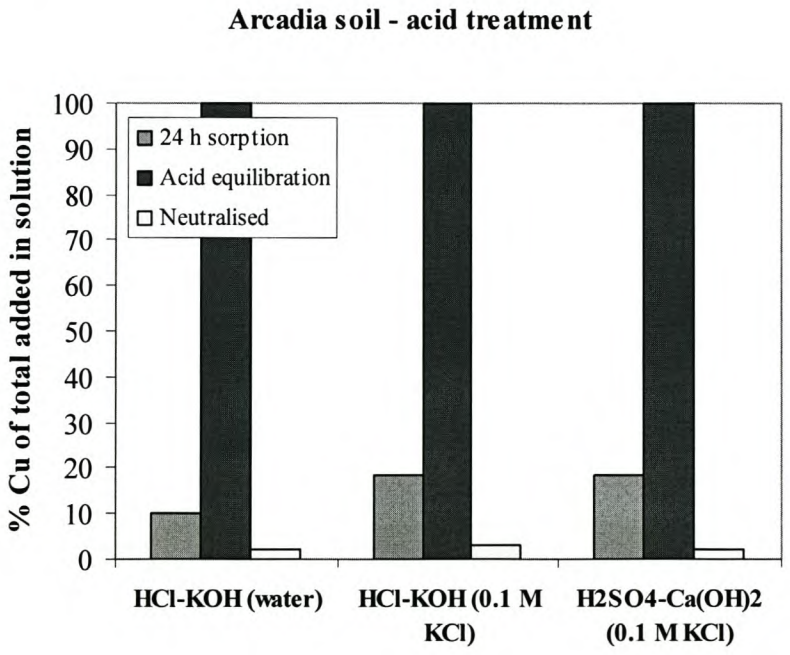


Figure 3.7 Percentage Cu of total Cu added in solution at the three stages in the acid treatment of the Arcadia soil.

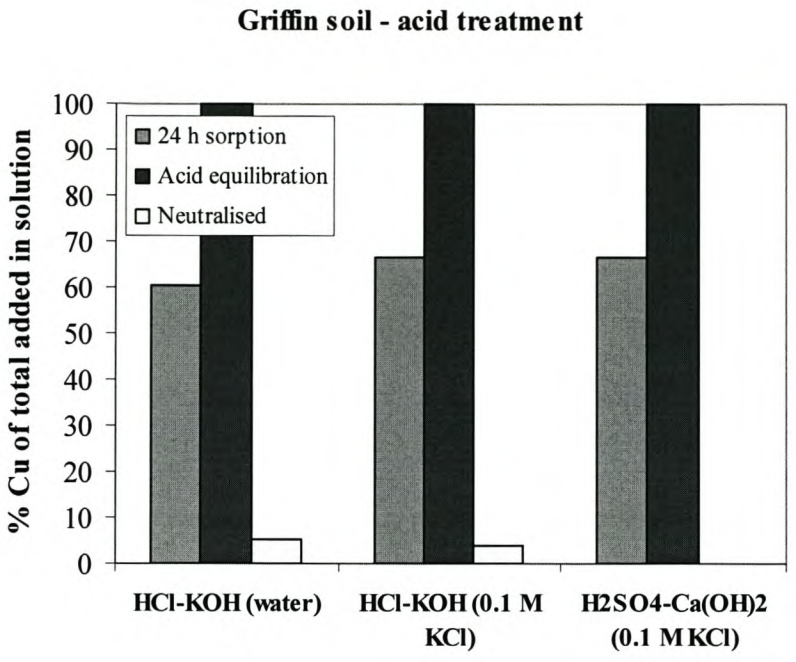


Figure 3.8 Percentage Cu of total Cu added in solution at the three stages in the acid treatment of the Griffin soil.

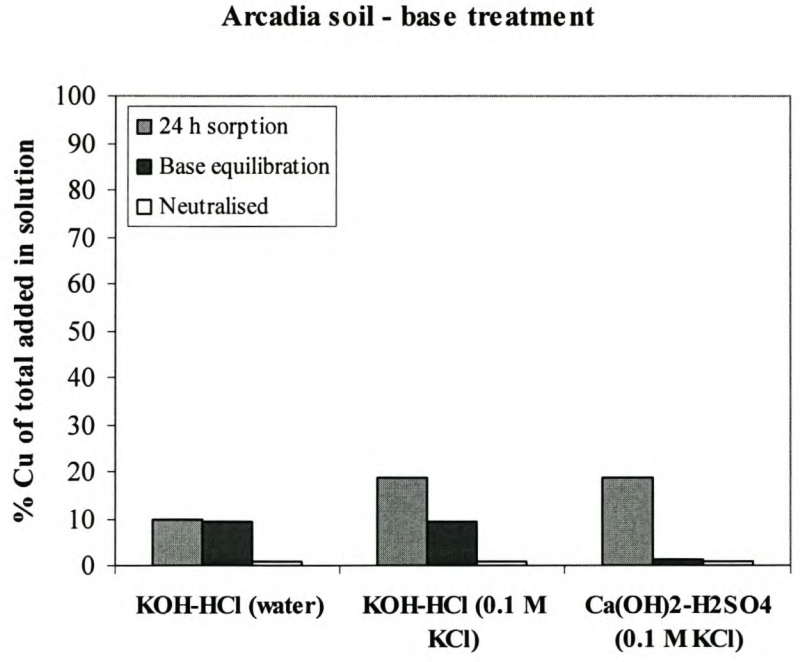


Figure 3.9 Percentage Cu of total Cu added in solution at the three stages of the base treatment of the Arcadia soil.

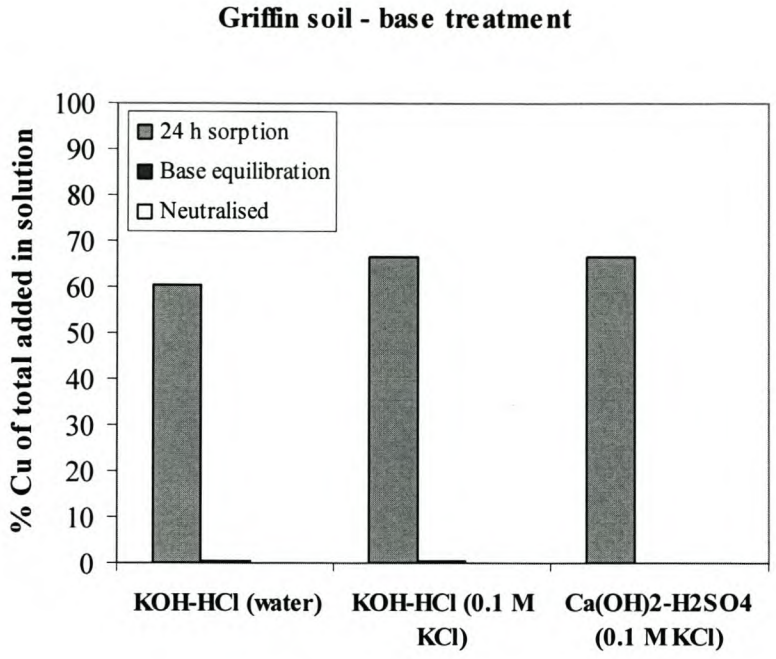


Figure 3.10 Percentage Cu of total Cu added in solution at the three stages in the base treatment of the Griffin soil.

Table 3.4 Mean Cu concentration (mmol.kg^{-1} soil) in solution at the three sampling stages of acid and base treatment of Arcadia and Griffin soils.

	Control	**Acid/base equilibration**	**Neutralisation**
	After 24 h shaking with Cu	After 7 days shaking	After filtration
	---------- mmol.kg^{-1} soil ----------		
Acid treatments			
Arcadia (HCl-KOH, water)	5.0	80.6	1.7
Arcadia (HCl-KOH, 0.1 M KCl)	10.0	82.0	2.5
Arcadia (H_2SO_4-$Ca(OH)_2$, 0.1 M KCl)	10.0	81.0	1.7
Griffin (HCl-KOH, water)	47.6	82.4	4.2
Griffin (HCl-KOH, 0.1 M KCl)	52.5	80.2	3.1
Griffin (H_2SO_4-$Ca(OH)_2$, 0.1 M KCl)	52.5	81.5	0.1
Base treatments			
Arcadia (KOH-HCl, water)	5.0	7.5	0.5
Arcadia (KOH-HCl, 0.1 M KCl)	10.0	7.4	0.7
Arcadia ($Ca(OH)_2$-H_2SO_4, 0.1 M KCl)	10.0	1.1	0.5
Griffin (KOH-HCl, water)	47.6	0.5	0.0
Griffin (KOH-HCl, 0.1 M KCl)	52.5	0.3	0.1
Griffin ($Ca(OH)_2$-H_2SO_4, 0.1 M KCl)	52.5	0.1	0.1

Table 3.5 provides a summary of the pH and EC changes measured during the acid and base treatments of the Arcadia and Griffin soils.

Table 3.5 Mean pH and EC ($dS.m^{-1}$) values of the Cu-treated Arcadia and Griffin soils at the three stages in the acid and base treatment.

Soil	Control		Acid/base equilibration		Neutralisation	
	After 24 h shaking with Cu		After 7 days shaking		Before filtration	
	pH	EC	pH	EC	pH	EC
Acid treatments						
Arcadia (HCl-KOH, water)	4.4	1.9	1.3	19.1	5.6	11.6
Arcadia (HCl-KOH, 0.1 M KCl)	4.2	13.6	1.3	29.0	5.6	20.8
Arcadia (H_2SO_4-$Ca(OH)_2$, 0.1 M KCl)	4.2	13.3	1.5	22.1	7.8	14.5
Griffin (HCl-KOH, water)	4.0	1.6	1.4	15.5	5.7	11.5
Griffin (HCl-KOH, 0.1 M KCl)	4.0	13.1	1.5	25.6	5.5	21.1
Griffin (H_2SO_4-$Ca(OH)_2$, 0.1 M KCl)	4.0	13.2	2.5	16.0	7.7	14.4
Base treatments						
Arcadia (KOH-HCl, water)	4.3	1.9	12.5	5.8	6.7	8.9
Arcadia (KOH-HCl, 0.1 M KCl)	4.2	13.4	12.4	16.4	6.5	18.6
Arcadia ($Ca(OH)_2$-H_2SO_4, 0.1 M KCl)	4.2	13.4	11.9	13.8	6.6	15.8
Griffin (KOH-HCl, water)	4.1	1.6	12.6	10.2	6.7	9.9
Griffin (KOH-HCl, 0.1 M KCl)	4.0	13.2	12.6	20.6	6.5	19.4
Griffin ($Ca(OH)_2$-H_2SO_4, 0.1 M KCl)	4.0	13.1	11.8	13.7	6.1	14.7

Both the acid and the base treatments were effective in removing Cu from solution, with almost all the Cu being removed (Table 3.4). The acid and base treatments seemed to be equally effective on both soils, however, the most dramatic effect of the acid and base treatments is seen on the Griffin soil, as there was a greater relative reduction in Cu from the initial sorption period to the final neutralisation stage (Figs 3.8 & 3.10). The base treatments appeared to be slightly more effective than the acid (Table 3.4). There was no significant difference in the effectiveness of the different acid-base pairs, even though it appears that the H_2SO_4-$Ca(OH)_2$ acid treatment on the Griffin soil resulted a more thorough removal of Cu (Fig. 3.8), this is probably only due to a pH effect, as the final pH of the neutralised sample was 2 units higher than that of the HCl-KOH treated samples (Table 3.5).

One interesting observation was that $Ca(OH)_2$ equilibrated Arcadia samples showed little organic matter solubilisation as the solution remained clear, whereas those samples treated

with KOH were black and cloudy. This is probably due to the presence of Ca^{2+} in $Ca(OH)_2$ treated samples which keeps the organic matter in a flocculated state. As seen in the first experiment in this chapter (Section 3.3.1), the acid equilibration resulted in all Cu becoming available in solution, whereas as the base equilibration resulted in most of Cu being removed from solution. The neutralisation of the base equilibrated samples resulted in a further decrease of available Cu, and this could indicate possible coprecipitation reactions. The presence of 0.1 M KCl background electrolyte also did not make a difference in the effectiveness of the treatments.

The mean EC values of the suspensions at the three stages during the acid and base treatments of the Cu-treated Arcadia and Griffin soils are shown in Fig. 3.11.

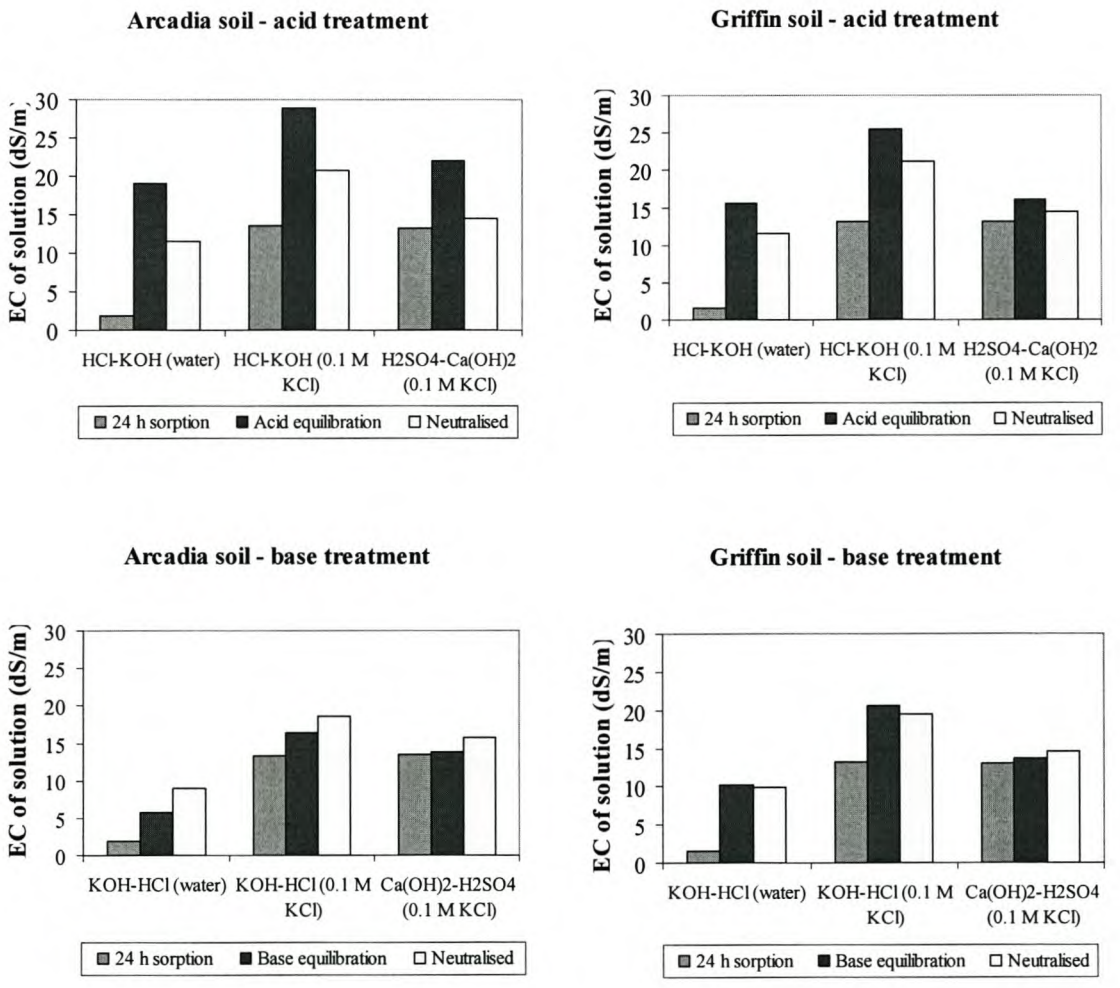


Figure 3.11 The mean suspension EC values ($dS.m^{-1}$) at the three stages in the acid and base treatments of the Cu –treated Arcadia and Griffin soils.

Much of the EC is due to the background electrolyte in the two treatments with 0.1 M KCl as background. However, it can still be seen that the final EC of all the acid treatments was lower than during the acid equilibration, this suggests that precipitation and/or sorption took place (Fig. 3.11). This observation was also made by Yeoh and Oades (1981b), where they neutralised a soil sample treated with phosphoric acid, and found a lower final EC. They related the amount of electrolyte in solution with the amount of exchangeable Al released. This suggests that the H_2SO_4 treatment did not result in as much exchangeable Al, probably due to the formation of Al-SO_4 complexes. Xu and Ji (2001) reported that H_2SO_4 had less of an acidifying effect on variable charge soils than HNO_3, due to the specific adsorption of SO_4^{2-} and the accompanied release of OH^-. They found that the difference in the effect of the acids was small for constant charge soils. This could also help explain why the pH of H_2SO_4 treated Griffin soil was much higher than that of the Arcadia after the 7-day equilibration period (Table 3.5).

The H_2SO_4-$Ca(OH)_2$ treated soils had a lower final EC than the HCl-KOH treated soils in 0.1 M KCl (Table 3.5). This final EC would have been lower still if the 0.1 M KCl background was absent. A lower EC could mean that a less soluble salt was generated, most likely gypsum ($CaSO_4$). Gypsum is most probably only likely to form in a field situation where the soil:solution ratio is much narrower, and facilitates precipitation. Thus it can be reasoned that H_2SO_4 and $Ca(OH)_2$ are a more practical choice of acid-base pair if this technique was to be applied in the field, as the salt generated could be considered effectively benign, unlike KCl or NaOH.

The base equilibrated samples had a higher final EC except in the case of the KOH-HCl treated Griffin soil (Fig. 3.11).

3.4 Conclusions

The efficacy of the acid and base treatments is dependent on the specific element, as it was shown that the method was effective in removing Cu from solution, but not Cd. Cu can form co-precipitates with Al hydroxide whereas Cd cannot due to its larger ionic radius. It was found that simply raising the pH (during the base equilibration period) resulted in the effective removal of Cd from solution. The acid and base treatments showed the most

dramatic results on the Cu-treated kaolinitic soil, where the amount of available Cu was reduced from approximately 70 % to 1% (Fig. 3.2).

The acid-base pair H_2SO_4 and $Ca(OH)_2$ was found to be equally effective as HCl and KOH in removing Cu from solution (Figs. 3.7 - 3.10). The addition of a 0.1 M KCl background electrolyte did also not have any effect on the final results of the treatments. As in the first experiment, the acid and base treatments showed the most dramatic results on the Griffin soil, where the fraction of Cu in solution of total added was reduced from 60% to between 4 and 0.1%, respectively.

The final solution EC of the H_2SO_4 and $Ca(OH)_2$ treated soils was lower than that of the HCl and KOH treated soils. It can be suggested that H_2SO_4 and $Ca(OH)_2$ are a more practical choice of acid-base pair, as the salt generated due to acid or base treatments in the field situation would most likely be gypsum, which does not have the harmful effects on the soil like NaCl or KCl. The use of H_2SO_4 would also make economic sense, as it is the cheapest commercially available strong acid.

We do not have direct evidence that the Cu coprecipitates with dissolved Al and Si, but it is likely, especially with acid priming, as Cu would not be able to precipitate as a separate Cu hydroxide phase, unlike at the high pH during base priming treatment. It would have been beneficial to determine the amount of Cu immobilised using a strong salt or EDTA extraction, as this might have given some indication to what extent the Cu was coprecipitated or specifically adsorbed onto mineral surfaces. Advanced spectroscopic methods, as demonstrated by Scheidegger *et al* (1997) would probably be able to give further indication of the nature and type of precipitates which form during these treatments.

GENERAL DISCUSSION

The aim of this project was to investigate the possibility of increasing a soil's specific adsorptive capacity or decontaminating metal treated soils using acid or base treatments. Acid or base priming can be described as subjecting the soil to harsh acid or base treatment for a period of time to allow dissolution to take place, and then neutralising the reaction products of dissolution, in order to create a new, more reactive surface in the soil.

In Chapter 1 soil dissolution using strong acid or base was investigated on four different soil types (organic; smectitic; sesquioxidic; kaolinitic), to obtain an idea of how much aluminium, silica and iron, can be released by the respective treatments and what the effect of clay mineralogy and organic matter content has on the reaction products. Acid dissolution resulted in much greater quantities of Al being released, than did base dissolution. It was found that an equilibration period of between one and two weeks of the soil in a 1:10 0.1 M HCl or KOH.suspension, allowed sufficient dissolution of Al and Si for the precipitation of new solids.

In Chapter 2 the effect of acid and base priming has on sorptive properties of soil was investigated on the same four soils used in dissolution studies in Chapter 1. Cadmium (II), copper (II) and phosphate sorption studies were carried out on primed and untreated soils, to investigate the change in sorption capacity of the soils due to acid or base priming. It was found that base priming increased Cd and Cu sorption in all of the soils, and this seems to be related to the amount of Al released during the dissolution phase and the final pH of the soil after neutralisation. Acid priming decreased Cd and Cu sorption in all soils, except the sesquioxidic sample, where there was also a notable increase. However, acid priming was found to increase phosphate adsorption in all the soils. Base priming also increased phosphate sorption, but not to the same extent as acid priming.

It was hypothesised that the composition of the dissolution products would affect newly formed precipitates, formed during the neutralisation step of acid or base priming. In particular, because Si is soluble at a high pH, it is likely that the precipitates formed from base priming would be hydroxyaluminosilicates, with possible permanent negative charge developing due to isomorphous substitution of tetrahedrally co-ordinated Al for Si, whereas,

those formed during acid priming would be mainly Al hydroxides. This could account for differences in the sorption properties of the treated soils.

Base priming could be recommended for reducing heavy metal mobility in the soil, while acid priming appeared to be completely ineffective. This was illustrated by the 1 M NH_4NO_3 extraction performed on the 12500 mg $Cd.kg^{-1}$ treated soils, whereby base priming resulted in up to 45% of sorbed Cd^{2+} being retained, whereas acid priming actually decreased it or resulted in no retention at all. It was also found that the variable charge soils showed a greater response to base priming than the smectitic soil, whereas the organic soil showed the greatest response to the acid priming treatment where phosphate sorption was concerned.

One of the shortcomings of this study is that pH was not fully taken into account during the sorption studies, and this is quite important as it has been well documented that HyA and HAS complexes which form on mineral surfaces increase the pH-dependant adsorption capacity of the soil (Saha *et al.,* 2001).

Further spectroscopic research is required to elucidate more of the structural nature of the precipitates formed during acid or base priming. Since they do not significantly alter the BET specific surface area of the soils, it would be interesting to find out exactly how they bind to the soil's surface and to what extent they are amorphous.

In Chapter 3 decontaminating metal-treated soils using acid and base treatments was investigated. Cadmium(II) and Cu(II) were chosen as contaminant metals and it was shown on both the smectitic and kaolinitic soils, that acid and base conditioning were only effective in removing Cu from solution. It was found that the acid-base pair H_2SO_4-$Ca(OH)_2$ proved equally effective as HCl and KOH in reducing Cu in solution. It can be expected that this acid-base pair would be of most practical importance as the salt generated is gypsum which is generally considered benign, and can actually help to improve the soil structure. The use of H_2SO_4 and $Ca(OH)_2$ would not only be more cost effective, compared to the use of other inorganic acids and bases, but also entails simpler handling.

It would have been more revealing if the acid and base treatments comparing the effectiveness of the acid-base pair H_2SO_4 and $Ca(OH)_2$ with HCl and KOH had been performed without a background electrolyte and in a narrower soil:solution ratio, such a

saturated paste, as the EC values would have been more meaningful and would have perhaps highlighted the difference in solubility of the generated KCl and gypsum.

Future research could include pot trials, where a bulk amount of soil is contaminated with a metal cation and then half of the contaminated soil could be acid or base-treated (using H_2SO_4 and $Ca(OH)_2$), while the rest remains untreated. A suitable plant could be grown in the treated and untreated soil to see to what extent these acid- or base-treated soils are decontaminated and whether they can support plant growth. It is likely that acid- and base-treated soils will have decreased CEC and increased specific adsorption of anions and cations. This could lead to poor fertility state and possibly some induced deficiencies of nutrients such as phosphate, and trace elements such as molybdenum and boron.

One of the aspects of applying these acid and base treatments to large quantities of soil in the field which needs to be assessed is self-neutralisation, which occurs as the soil buffers the addition of strong acid or base. This can be exploited to some extent as it means that less counter-acid or -base is required to neutralise acidified or alkalised soil, as if left over a long enough period of time the pH will return to almost the original pH of the soil. It does however, also make it more difficult to uniformly control the pH of the soil, which would make applying the treatments more difficult.

Advanced spectroscopic investigation (Scheidegger *et al.,* 1997) could possibly elucidate to what extent metals are coprecipitated with Al or Fe during acid or base treatment of contaminated soil.

Activation of soils by acid or base treatments could have some useful applications in decontaminating soils or decreasing the mobility of inorganic contaminants in soils. One problem associated with the technique is the large amount of salt generated during the neutralisation of the added acid or base. This problem can be minimised by using H_2SO_4 and $Ca(OH)_2$, as gypsum would be the final reaction product. Primed soils could also be used as cheap adsorbents for decontaminating water, specifically in removing harmful anions from solution such as arsenate, molybdate, urananate, vanedate or fluoride.

REFERENCES

Arbeitsgemeinschaft Bodenkunde. 1994. Bodenkundliche Kartieranleitung, Hannover, Germany.

Barnhisel, R.I. 1977. Chlorites and hydroxy interlayered vermiculite and smectite. In: Dixon, J.B. and Weed, S.B. (eds), Minerals in soil environments. Soil Science Society of America, Madison, USA, pp 331-350.

Bowden, J.W., Posner, A.M. and Quirk, J.P. 1980. Adsorption and charging phenomena in variable charge soils. In: Theng, B.K.G. (ed) Soils with variable charge. New Zealand Society of Soil Science.

Brown, G. and Gustache, M.C. 1967. Mixed magnesium-aluminium hydroxides II. Structure and structural chemistry of synthetic hydroxycarbonates and related minerals and compounds. *Clay Minerals* 7:193-201.

Bruggenwert, M.G.M., Hiemstra, T. and Bolt, G.H. 1991. Proton sinks in controlling soil acidification. In: Ulrich, B. and Sumner, M.E. (eds), Soil acidity. Springer-Verlag, Berlin, pp 8-27.

Chidambaram, S., Ramanathan, A.L. and Vasudevan, S. 2003. Fluoride removal studies in water using natural materials. *Water SA* 29:339-345.

Coetzee, P.P., Coetzee, L.L., Puka, R. and Mubenga, S. 2003. Characterisation of selected South African clays for defluoridation of natural waters. *Water SA* 29:331-338.

Fey, M.V. and le Roux, J. 1975. Electric charges on sesquioxidic soil clays. *Soil Science Society of America Journal* 40:359-364.

Ford, R.G., Scheinhost, A.C. and Sparks, D.L. 2001. Frontiers in metal sorption/precipitation mechanisms on soil mineral surfaces. *Advances in Agronomy* 74:41-62.

Garcia-Sanchez, A., Alvarez-Ayuso, E. and Jimenez de Blas, O. 1999. Sorption of heavy metals from industrial waste water by low-cost mineral silicates. *Clay Minerals* 34:469-477.

Garcia-Sanchez, A., Alvarez-Ayuso, E. and Rodriguez-Martin, F. 2002. Sorption of As(V) by some oxyhydroxides and clay minerals. Application to its immobilization in two polluted mining soils. *Clay Minerals* 37:187-194.

Garrido, F., Illera, V., Vizcayno, C. and García-González, M.T. 2003. Evaluation of industrial by-products as soil acidity amendments: chemical and mineralogical implications. *European Journal of Soil Science* 54:411-422.

Gee, G.W. and Bauder, J.W. 1986. Particle size analysis. In: Klute, A. (ed) Methods of soil analysis, No 9, Part 1. American Society of Agronomy, Madison, USA.

Gustache, M.C., Brown, G. and Mortland, M.M. 1967. Mixed magnesium-aluminium hydroxides I. Preparation and characterization of compounds formed in dialysed systems. *Clay Minerals* 7:177-192.

Hansen, H.C.B. and Taylor, R.M. 1990. Formation of synthetic analogues of double metal-hydroxy carbonate minerals under controlled pH conditions: I. The synthesis of pyroaurite and reevsite. *Clay Minerals* 25:161-179.

Harsh, J.B. and Doner, H.E. 1984. Specific adsorption of copper on a hydroxyaluminum-montmorillonite complex. *Soil Science Society of America Journal* 48:1034-1039.

Harter, R.D. and Naidu, R. 1995. Role of metal-organic complexation in metal sorption by soils. *Advances in Agronomy* 55:219-263.

Hunter, R.J. 1981. Zeta potential in colloid science, principles and applications. Academic Press, Sydney.

Inoue, K. and Satoh, C. 1993. Surface charge characteristics of hydroxyaluminosilicate- and hydroxyaluminum-montmorillonite complexes. *Soil Science Society of America Journal* 57:545-552.

Janssen, R.P.T., Bruggenwert, M.G.M. and Riemsdijk, W.H. 2003a. Effect of Al hydroxide polymers on cation exchange of montmorillonite. *European Journal of Soil Science* 54:335-345.

Janssen, R.P.T., Bruggenwert, M.G.M. and Riemsdijk, W.H. 2003b. Zinc ion adsorption on montmorillonite – Al hydroxide polymer systems. *European Journal of Soil Science* 54:347-355.

Kaiser, K. and Guggenberger, G. 2003. Mineral surfaces and soil organic matter. *European Journal of Soil Science* 54:219-236.

Kinniburgh, D.G., Jackson, M.L. and Syers, J.K. 1976. Adsorption of alkaline earth, transition, and heavy metal cations by hydrous oxide gels of iron and aluminium. *Soil Science Society of America Journal* 40:796-799.

Lahodny-Šarc, O. and Dragčević, Z. 1981. The influence of complex-forming agents on the structure of precipitated aluminium hydroxide. *Proceedings of the International Clay Conference*. 14:529-535.

Lindsay, W.L. 1979. Chemical equilibria in soils. John Wiley & Sons, Inc., New York.

Lothenbach, B., Furrer, G. and Schulin, R. 1997. Immobilization of heavy metals by polynuclear aluminium and montmorillonite compounds. *Environmental Science and Technology* 31:1452-1462.

Lothenbach, B., Krebs, R., Furrer, G., Gupta, S.K. and Schulin, R. 1998. Immobilization of cadmium and zinc in soil by Al-montmorillonite and gravel sludge. *European Journal of Soil Science* 49:141-148.

Marion, G.M., Black, C.H. And Zedler, P.H. 1989. The effect of extreme HCl deposition on soil acid neutralization following simulated shuttle rocket launches. *Water, Air and Soil Pollution* 43:345-363.

McBride, M.B. 1994. Environmental chemistry of soils. Oxford University Press, New York.

McKeague, J.A. and Cline, M.G. 1963. Silica in soils. *Advances in Agronomy* 15:339-396.

O'Neill, P. 1995. Arsenic. In: Alloway, B.J.(ed) Heavy metals in soils. Blackie Academic & Professional, U.K.

Parfitt, R.I. 1980. Chemical properties of variable charge soils. In: Theng, B.K.G. (ed) Soils with variable charge. New Zealand Society of Soil Science.

Rich, C.I. 1960. Aluminum interlayers of vermiculites. *Science Society of America Proceedings* 24:26-32.

Ritchie, G.S.P. 1994. Role of dissolution and precipitation of minerals in controlling soluble aluminium in acidic soils. *Advances in Agronomy* 53:47-83.

Robert, M. and Terce, M. 1987. Effect of gels and coatings on clay mineral chemical properties. In: Bar-Yosef, N.J., Barrow, N.J. and Goldshmid, J. (eds.), Inorganic contaminants in the vadose zone. Ecological Studies vol. 74:57-71. Springer-Verlag, U.S.A.

Rowell, D.L. 1993. Soil science: methods and applications. Longman Publishers, U.S.A.

Ruiz-Cruiz, M.D. and Moreno-Real, L. 1991. Practical determination of allophane and synthetic alumina and iron oxide gels by x-ray diffraction. *Clay Minerals* 26:377-387.

Saha, U.K., Hirdate, S. and Inoue, K. 1998. Retention of phosphate by hydroxyaluminosilicate- and hydroxyaluminum-montmorillonite complexes. *Soil Science Society of America Journal* 62:922-929.

Saha, U.K., Taniguchi, S. and Sakurai, K. 2001. Adsorption behaviour of cadmium, zinc and lead on hydroxyaluminum- and hydroxyaluminosilicate-montmorillonite complexes. *Soil Science Society of America Journal* 65:694-703.

Saha, U.K., Taniguchi, S. and Sakurai, K. 2002. Simultaneous adsorption of cadmium, zinc and lead on hydroxyaluminum- and hydroxyaluminosilicate-montmorillonite complexes. *Soil Science Society of America Journal* 66:117-128.

Sakurai, K and Huang, P.M. 1998. Intercalation of hydroxy-aluminosilicate and hyrdroxy-aluminum in montmorillonite and resultant physicochemical properties. *Soil Science Society of America Journal* 62:362-368.

Schulthess, C.P. and Huang, C.P. 1990. Adsorption of heavy metals by silicon and aluminium oxide surfaces on clay minerals. *Soil Science Society of America Journal* 54:679-688.

Scheidegger, A.M. and Sparks, D.L. 1996. A critical assessment of sorption-desorption mechanisms at the soil mineral/water interface. *Soil Science* 161:813-831.

Scheidegger, A.M., Lamble, G.M. and Sparks, D.L. 1997. Spectroscopic evidence for the formation of mixed-cation hydroxide phases upon metal sorption on clays and aluminium oxides. *Journal of Colloid and Interface Science* 186:118-128.

Schofield, R.K. 1949. Effect of pH on electric charges carried by clay particles. *Journal of Soil Science* 1:1-8.

Schwertmann, U. and Jackson, M.L. 1964. Influence of hydroxy aluminium ions of pH titration curves of hydronium-aluminum clays. *Science Society of America Proceedings* 28:179-183.

Senkayi, A.L., Dixon, J.B. and Hossner, L.R. 1981. Simulated weathering of lignite overburden shales from Northeast Texas. *Soil Science Society of America Journal* 45:982-986.

Soil Classification Working Group. 1991. Soil classification: a taxonomic system for South Africa. Department of Agricultural Development, South Africa.

Sparks, D.L. 1995. Enviromental soil chemistry. Academic Press, USA.

Sumner, M.E. 1963. The effect of iron oxides on positive and negative charges in clays and soils. *Clay Minerals Bulletin* 5:218-226.

Taylor, R.M. 1984. The rapid formation of crystalline double hydroxy salts and other compounds by controlled hydrolysis. *Clay Minerals* 19:591-603.

Thevenot, F., Szymanski,R and Chaumette, P. 1989. Preparation and characterization of Al-rich and Zn-Al hydrotalcite-like compounds. *Clays and Clay Minerals* 37:396-402.

Veerhoff, M. and Brümmer, G.W. 1993. Bildung schlechtkristalliner bis amorpher Verwitterungsprodukte in stark bis extrem versauerten Waldböden. Zeitschrift für Pflanzenernährung und Bodenkunde 156:11-17.

Violante, A. and Violante, P. 1980. Influence of pH, concentration, and chelating power of organic anions on the synthesis of aluminium hydroxides and oxyhydroxides. *Clays and Clay Minerals* 28:425-434.

Wang, Y. and Reardon, E.J. 2001. Activation and regeneration of a soil for defluoridation of drinking water. *Applied Geochemistry* 16:531-539.

Wilson, M.A., McCarthy, S.A. and Fredericks, P.M. 1986. Structure of poorly-ordered aluminosilicates. *Clay Minerals* 21:879-897.

Ulrich, B. 1991. An ecosystem approach to acidification. In: Ulrich, B. and Sumner, M.E. (eds), Soil acidity. Springer-Verlag, Berlin, pp 50-56.

Usman, A.R.A., Kuzyakov, Y. and Stahr, K. 2002. Sorption and immobilization of Pb, Cd and Zn by artificial soil and by sludge-contaminated soil after addition of clay minerals. Unpublished at the time.

Wada, S. and Wada, J. 1980. Formation, composition and structure of hydroxy-aluminosilicate ions. *Journal of Soil Science* 31:457-467.

Xu, R.K. and Ji, G.L. 2001. Effects of H_2SO_4 and HNO_3 on soil acidification and aluminium speciation in variable and constant charge soils. *Water, Air, and Soil Pollution* 129:1-4.

Yeoh, N.S. and Oades, J.M. 1981. Properties of soils and clays after acid treatment. I Clay minerals. *Australian Journal of Soil Research* 19:147-158.

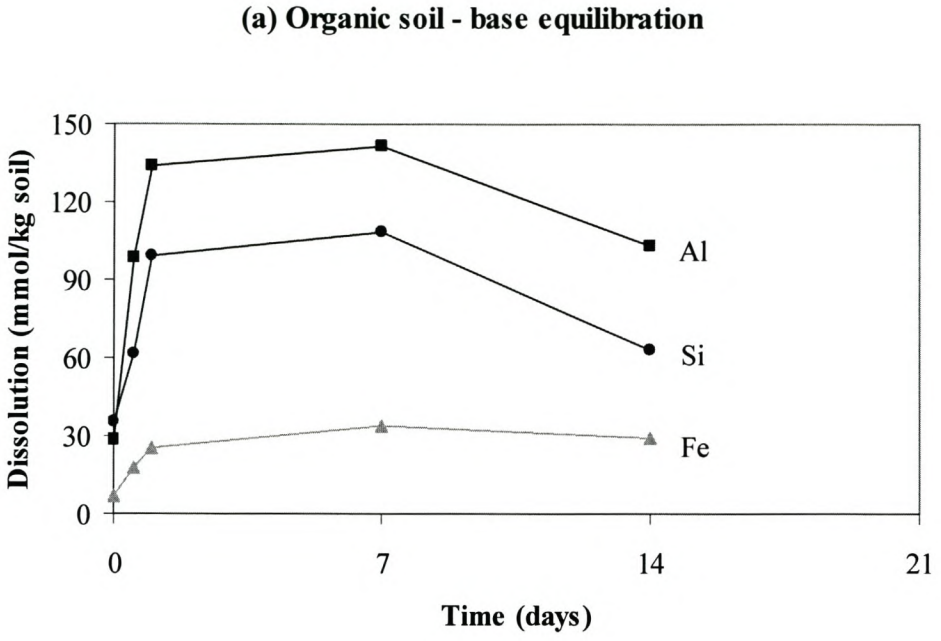
Yeoh, N.S. and Oades, J.M. 1981. Properties of soils and clays after acid treatment. II Urrbrae fine sandy loam. *Australian Journal of Soil Research* 19:159-166.

Yokoyama, T., Ueda, A., Kato, K., Mogi, K. and Matsuo, S. 2002. A study of the alumina-silica gel adsorbent for the removal of silicic acid from geothermal water: Increase in adsorption capacity of the adsorbent due to formation of amorphous aluminosilicate by adsorption of silicic acid. *Journal of Colloid and Interface Science* 243:1-5.

APPENDIX 1 – Supplementary data from Chapter 1

Table A1.1 Tabulated pH values at the various sampling intervals during acid- and base-equilibration of soils over the 35-day period.

Soil treatment	Sampling stage					
	Initial	**12 hours**	**1 day**	**7 days**	**14 days**	**35 days**
Acid-equilibrated						
Organic	1.4	1.3	1.4	1.5	1.6	1.7
Smectitic	1.4	1.4	1.4	1.7	1.8	2.0
Sesquioxidic	1.3	1.3	1.4	1.7	2.1	2.6
Kaolinitic	1.1	1.2	1.2	1.2	1.3	1.3
Base-equilibrated						
Organic	12.6	12.6	12.5	12.5	12.3	12.1
Smectitic	12.8	12.8	12.9	13.0	12.8	12.9
Sesquioxidic	12.7	12.7	12.8	12.9	12.8	12.8
Kaolinitic	13.1	13.0	13.0	12.8	12.9	13.0



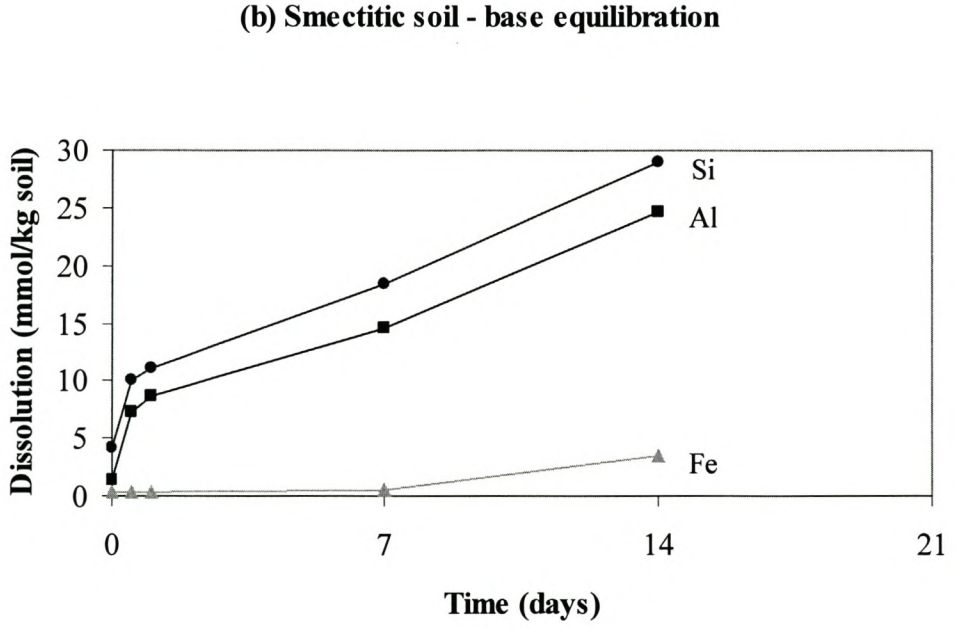


Figure A1.1 Repeated base equilibration of (a) organic and (b) smectitic soils showing the dissolution (expressed per unit mass of soil) of Al, Si and Fe over 14 day period.

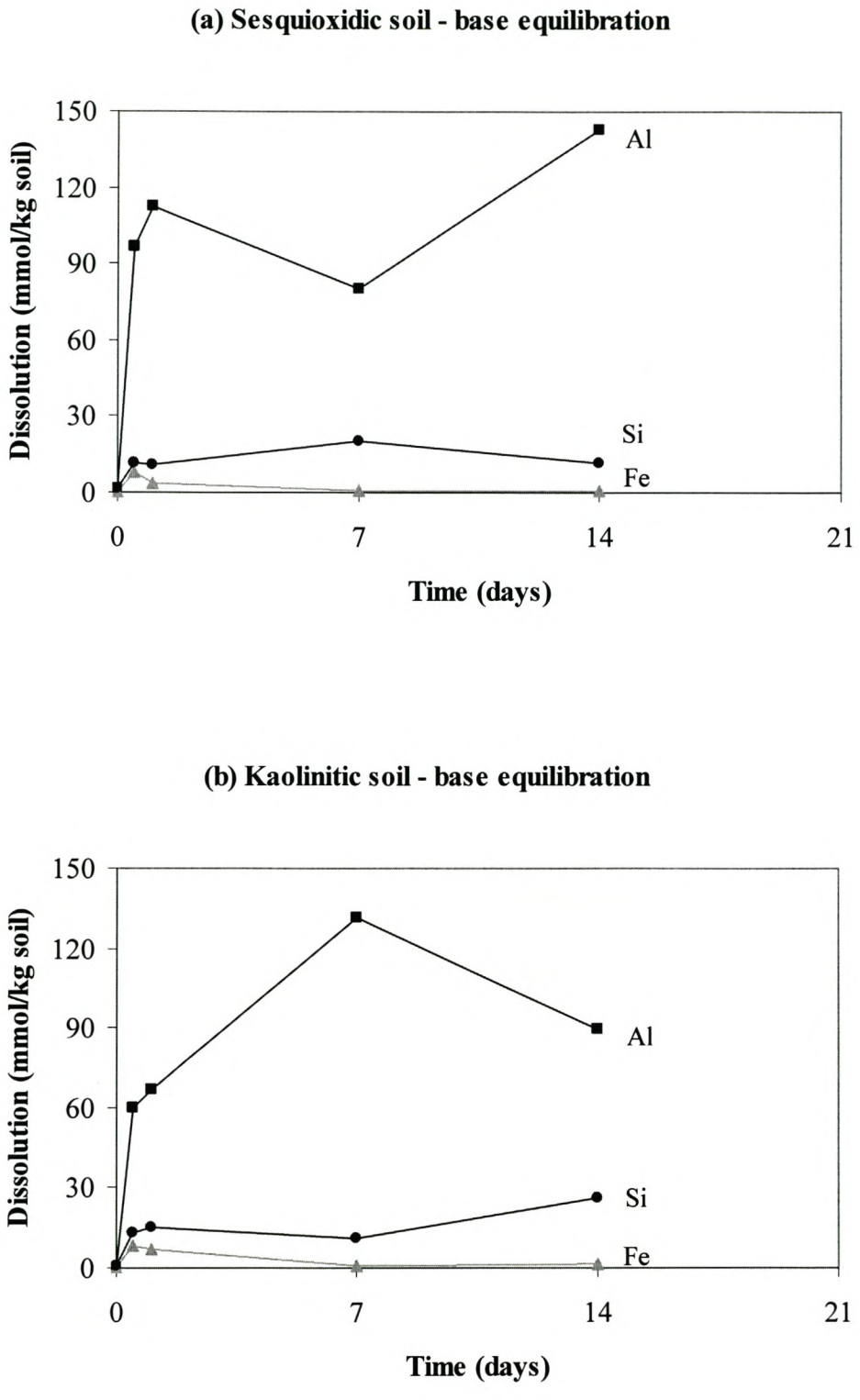


Figure A1.2 Repeated base equilibration of (a) sesquioxidic and (b) kaolinitic soils showing the dissolution (expressed per unit mass of soil) of Al, Si and Fe over 14 day period.

APPENDIX 2 – Supplementary data from Chapter 2

Table A2.1 Final EC values ($dS.m^{-1}$) of the primed soils after repeated washing in 1:10 soil to solution ratio, in comparison to untreated soil.

	Untreated	Acid-primed	Base-primed
Organic	88	18	65
Smectitic	118	39	18
Sesquioxidic	4	13	10
Kaolinitic	10	24	18

Table A2.2 Repeatability of Cd measured in solution using flame AAS ($mg.l^{-1}$) for the Cd sorption study on the organic acid-, base-primed and untreated soil.

Cd Treatment (mg/l)	Dilution factor	Replicate 1 Conc. in diluted solution (mg/l)	Replicate 2 Conc. in diluted solution (mg/l)
Organic soil - untreated			
20	5	0.276	0.335
50	5	0.880	0.886
100	100	0.169	0.238
200	100	0.572	0.562
500	1000	0.262	0.279
Organic soil – acid-primed			
20	10	0.058	0.062
50	10	0.216	0.203
100	100	0.135	0.135
200	100	0.532	0.539
500	1000	0.317	0.315
Organic soil – base-primed			
20	10	0.119	0.132
50	10	0.421	0.399
100	100	0.079	0.086
200	100	0.182	0.192
500	1000	0.779	0.765

Table A2.3 Repeatability of the Cu measured in solution using ICP-MS ($mg.l^{-1}$) for the Cu sorption study on the sesquioxidic acid-, base-primed and untreated soil.

Cu Treatment (mg/l)	Replicate 1 Conc. in solution (mg/l)	Replicate 2 Conc. in solution (mg/l)
Sesquioxidic soil - untreated		
100	53.31	50.28
200	141.20	147.87
500	439.14	447.64
1000	959.01	981.98
Sesquioxidic soil – acid-primed		
100	18.79	16.14
200	101.34	102.88
500	397.23	392.25
1000	909.51	902.68
Sesquioxidic soil – base-primed		
100	5.06	1.51
200	8.68	7.94
500	263.97	263.22
1000	785.05	793.10

Table A2.4 Repeatability of the 1 M NH_4NO_3 extraction of Cd on the 12500 $mg.kg^{-1}$ soil Cd-treated soils determined using flame AAS.

Treatment	Dilution factor	Replicate 1 Conc. in diluted solution (mg/l)	Replicate 2 Conc. in diluted solution (mg/l)
Organic acid-primed	1000	0.213	0.206
Organic base-primed	1000	0.243	0.246
Organic untreated	1000	0.243	0.243
Smectitic acid-primed	1000	0.230	0.237
Smectitic acid-primed	1000	0.234	0.229
Smectitic untreated	1000	0.220	0.215
Sesquioxidic acid-primed	1000	0.144	0.144
Sesquioxidic base-primed	1000	0.230	0.177
Sesquioxidic untreated	1000	0.113	0.118
Kaolinitic acid-primed	1000	0.108	0.110
Kaolinitic base-primed	1000	0.160	0.159
Kaolinitic untreated	1000	0.102	0.102

Table A2.5 Tabulation of the pH data of Hohenheim soils performed in 1 M KCl, 0.1 M KCl and 0.01 M KCl from the surface charge determination study.

Soil	pH 1:100 1 M KCl	pH 1:100 0.1 M KCl	pH 1:100 0.01 M KCl
Organic			
Untreated	4.14	4.36	4.86
Acid-primed	4.30	4.41	5.04
Base-primed	5.34	5.77	6.27
Smectitic			
Untreated	6.14	6.68	6.91
Acid-primed	5.93	6.43	6.84
Base-primed	7.30	8.01	8.43
Sesquioxidic			
Untreated	4.67	4.88	5.39
Acid-primed	5.53	6.27	6.49
Base-primed	6.19	7.08	7.50
Kaolinitic			
Untreated	4.77	4.90	5.04
Acid-primed	4.92	5.00	5.40
Base-primed	5.97	6.45	7.15

APPENDIX 3 – Supplementary method description and data from Chapter 3

Method of clay separation for XRD glass slide preparation:

Approximately 50 g soil was taken and made into a slurry with distilled water in a 250 ml plastic bottle. The pH of the slurry was adjusted with $NaHCO_3$ to about pH 10 and this was shaken for 3-4 hours. After shaking overnight the slurries were placed in 5 l buckets and topped up with tap water. The suspensions were allowed to stand for 16 h when the top 18 cm were siphoned off. This contained the clay fraction. 1 M HCl was then added to the clay suspensions to adjust the pH to 5-6 to induce the flocculation of the clay. $MgSO_4$ was added to the arcadia sample to make it up to a 1 M solution. KCl was added to the griffin sample also to make it up to a 1 M solution. This was then shaken by hand for a few minutes and allowed to stand. After a few hours the excess water was siphoned off. The arcadia and griffin samples were then centrifuged and then shaken with 1 M $MgSO_4$ and 1 M KCl solutions to ensure Mg and K saturation respectively. The samples were then centrifuged again, and the excess fluid was poured off. The samples were then washed twice with a 1:1 water and ethanol mixture and centrifuged. After the washing the clays were placed in dialysis tubing and were dialysed in water for a period of 10 days until the bathwater tested free from chloride. The clays were then smeared on glass plates and allowed to air dry. Figs A3.1 & A3.2 show the x-ray diffractograms of the Arcadia and Griffin clay samples.

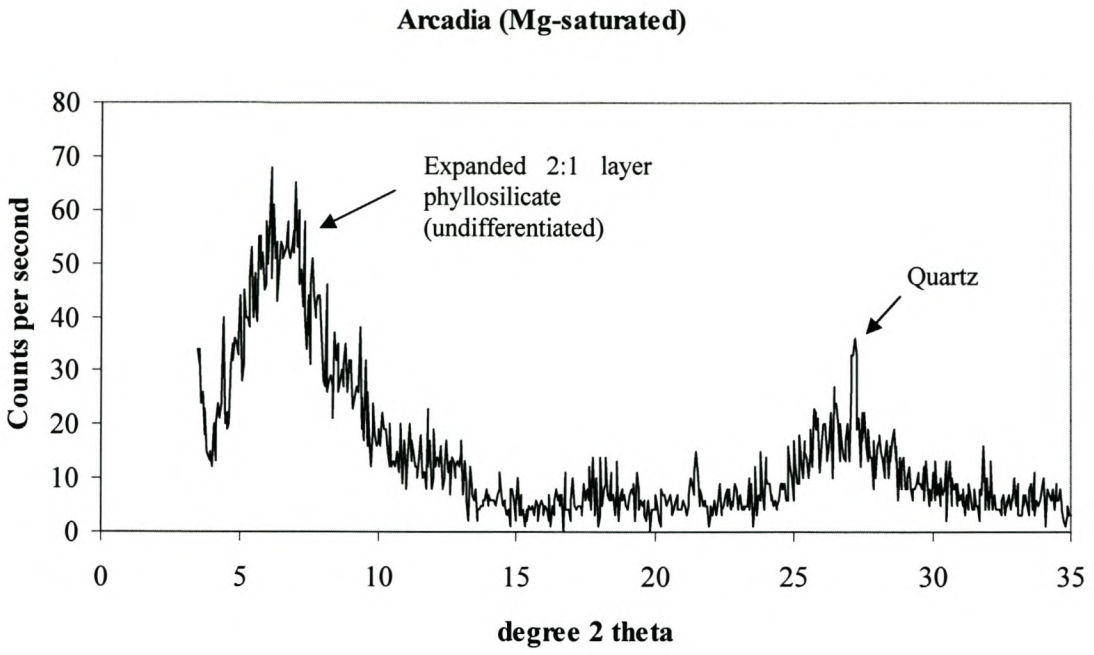


Figure A3.1 X-ray diffractogram of the Mg-saturated Arcadia clay.

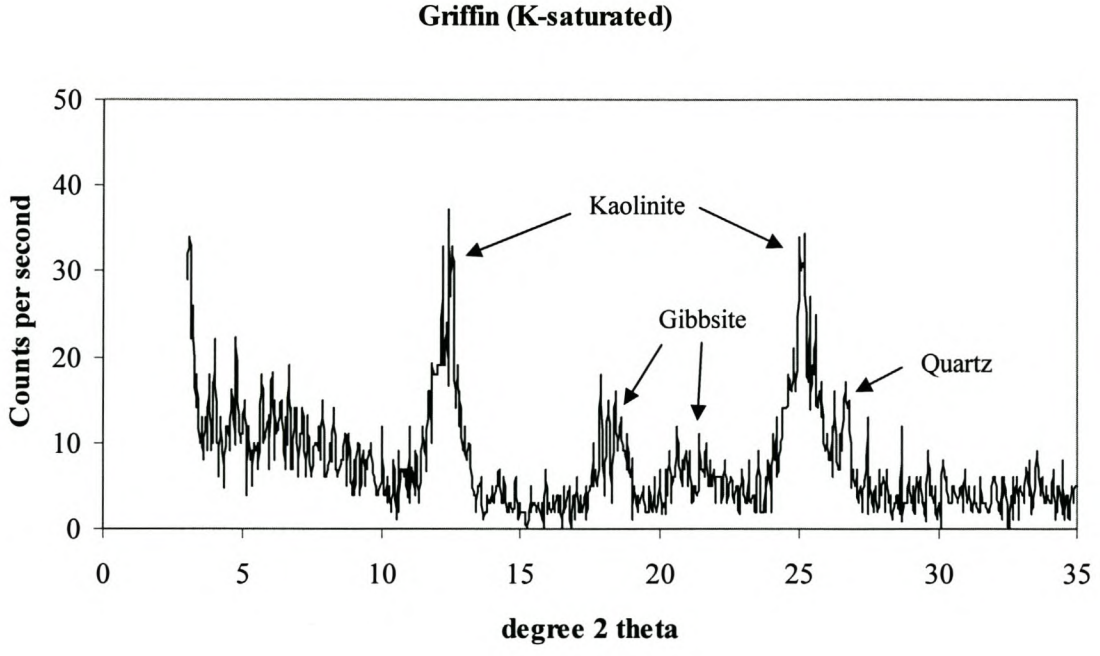


Figure A3.2 X-ray diffractogram of K-saturated Griffin clay.

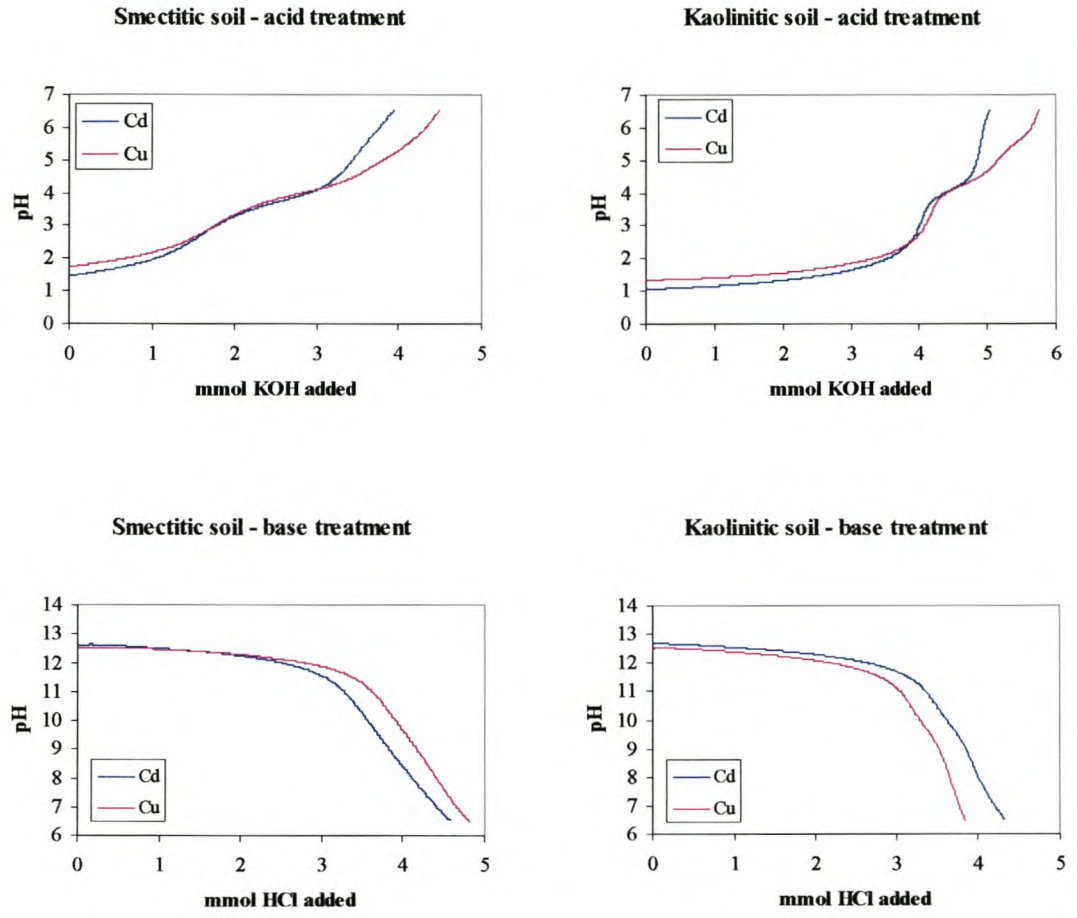


Figure A3.3 Neutralisation titration curves of the acid- and base-equilibrated Cd- and Cu-treated smectitic and kaolinitic soils.

Table A3.1 Repeatability of the Cd, Al and Si determinations in solution using ICP-OES of the acid and base treatments of the Cd-treated smectitic soil.

Treatment stage	**Concentration in solution**								
	Cd (mg/l) Replicate			**Al (mg/l) Replicate**			**Si (mg/l) Replicate**		
	1	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**
Acid treatment									
Sorption period	52.1	53.4	53.2	<0.5	<0.5	<0.5	0.81	0.82	0.75
Acid equilibration	481.6	498.9	433.3	440.2	446.4	436.4	337.0	342.5	333.5
Neutralised to pH 6.5	219.8	-	-	1.8	-	-	33.9	-	-
Base treatment									
Sorption period	52.1	53.4	53.2	<0.5	<0.5	<0.5	0.81	0.82	0.75
Base equilibration	0.72	0.73	0.72	5.65	5.44	5.69	4.86	4.62	4.92
Neutralised to pH 6.5	67.0	-	-	<0.5	-	-	1.40	-	-

Table A3.2 Repeatability of the Cu, Al and Si determinations in solution using ICP-OES of the acid and base treatments of the Cu-treated smectitic soil.

Treatment stage	Concentration in solution								
	Cu (mg/l) Replicate			Al (mg/l) Replicate			Si (mg/l) Replicate		
	1	2	3	1	2	3	1	2	3
Acid treatment									
Sorption period	42.9	41.0	40.4	<0.5	<0.5	<0.5	2.36	2.43	2.51
Acid equilibration	389.1	396.9	400.7	45.0	45.0	45.5	34.3	34.5	34.8
Neutralised to pH 6.5	2.76	-	-	<0.5	-	-	4.0	-	-
Base treatment									
Sorption period	42.9	41.0	40.4	<0.5	<0.5	<0.5	2.36	2.43	2.51
Base equilibration	10.6	10.6	10.6	4.16	4.41	4.30	5.11	5.62	5.57
Neutralised to pH 6.5	4.19	-	-	<0.5	-	-	0.85	-	-

Table A3.3 Comparison of ICP-OES and ICP-MS readings of selected Cd and Cu concentrations in supernatants of acid and base treatments of smectitic and kaolinitic soils.

Treatment	Cd (mg/l)		Cu (mg/l)	
	ICP-OES	ICP-MS	ICP-OES	ICP-MS
Smectitic soil				
Acid - Neutralised to pH 6.5			275.5	305.8
Base - Base equilibration	0.725	0.743		
Kaolinitic soil				
Acid - Neutralised to pH 6.5			595.0	642.5
Base - Base equilibration	2.488	2.260		
Base - Neutralised to pH 6.5			1.035	1.090

Table A3.4 Repeatability of Cu determinations in solution ($mg.l^{-1}$) using flame AAS at the sampling stages in acid and base treatments on Arcadia and Griffin soils.

	Control		**Acid/base equilibration**		**Neutralisation**	
	After 24 h shaking with metal		After 7 days shaking		After filtration	
	Replicate					
	1	**2**	**1**	**2**	**1**	**2**
Acid treatments						
Arcadia (HCl-KOH, water)	26	38	506	470	11	9
Arcadia (HCl-KOH, 0.1 M KCl)	62	86	767	495	13	16
Arcadia (H_2SO_4-$Ca(OH)_2$, 0.1 M KCl)	-	-	508	473	10	-
Griffin (HCl-KOH, water)	278	-	502	495	12	36
Griffin (HCl-KOH, 0.1 M KCl)	321	353	515	505	2	3
Griffin (H_2SO_4-$Ca(OH)_2$, 0.1 M KCl)	-	-	517	470	0.4	0.2
Base treatments						
Arcadia (KOH-HCl, water)	54	53	47	44	3	3
Arcadia (KOH-HCl, 0.1 M KCl)	105	111	44	45	4	4
Arcadia ($Ca(OH)_2$-H_2SO_4, 0.1 M KCl)	-	-	7	6	3	3
Griffin (KOH-HCl, water)	291	338	3.5	2.1	0.2	0.2
Griffin (KOH-HCl, 0.1 M KCl)	319	341	2	2	0.6	0.2
Griffin ($Ca(OH)_2$-H_2SO_4, 0.1 M KCl)	-	-	0.7	0.5	0.5	0.7